CALCULATION OF THE ELECTRONIC STRUCTURE OF THE U CENTER AND RELATED COLOR CENTERS IN ALKALI HALIDES BY USING THE MULTIPLE SCATTERING METHOD

By

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The spin-polarized multiple scattering Xα self-consistent field method has been applied to the problem of color centers in ionic crystal. Within the muffin-tin approximation, the electronic structures of the U and F centers in several alkali halides and the U_1 and U_2 centers in potassium chloride have been calculated and studied using a cluster of ions including the first nearest-neighbors. From the transition state calculation, the U and F center optical absorption energies in several alkali halides are found to be in good agreement with experiment except in the case of a crystal with a very small interionic distance. In the U_2 center case, two possible transitions are investigated and one transition agrees well with experiment while the other, a charge transfer process, gives an energy too small. The hyperfine

interaction of the U_2 center and the optical absorption of the U_1 center have also been studied.

Larger clusters including the second nearest-neighbors and the third nearest-neighbors for the U and F centers in KCl have been calculated and the absorption energies are found to oscillate with the size of the cluster. This problem has been investigated and discussed by comparing the cluster calculation of the pure KCl crystal with the energy band calculation and the experimental data. One of the improvements for the large cluster calculation is a more accurate crystalline potential. In the present calculation this potential is calculated from a point-ion assumption.

CHAPTER I

INTRODUCTION

Color centers in alkali halide crystals have been observed and studied for many years. But the calculation of the electronic structure and the properties of the color center or impurity in solid is difficult because of the complexity of the system involved. Thus, most of the studies are done by methods that are semi-empirical in nature.

Recently, the Xα method (Slater, 1972; Slater and Johnson, 1972) which makes use of the so-called Xα statistical exchange, has been successfully applied to many problems. For molecules, the multiple scattering Xα self-consistent field (MS-Xα-SCF) method (Johnson, 1973) gives satisfactory results in many cases and is also very efficient in computing time. Thus, one of the purposes of the present dissertation is to study the electronic structure of color centers by direct calculation of the properties of a cluster of ions using the MS-Xα-SCF method. From the calculation the optical absorption process of the color center can be studied and the transition energy can be calculated.

Several clusters with different sizes were used in the calculation, but only one cluster (Figure 2.1) is used for extensive study of the U center from LiF to KBr. Other color centers (F, U_1 and U_2 centers) are studied mainly in the KCl

crystal. From these investigations, the capability and limitation of the present approach can be checked.

Another purpose of this dissertation is to compare the present cluster calculation of a pure crystal with energy band calculations and the experimental data. From this comparison, the characteristics of the present cluster method and possible improvements on the method for future applications can be found.

CHAPTER II

COLOR CENTERS IN ALKALI HALIDES

2.1 Optical Absorption

The alkali halides are, in many respects, ideal crystals for theoretical and experimental studies. They have cubic structure and many of their properties are affected by the strong Coulomb interactions which, in turn, are due to the highly ionic nature of these crystals. For a pure alkali halide crystal, the energy gap between the conduction band and the valence band is of the order of 10 eV. This corresponds to a light quantum in the far ultraviolet and, hence, the crystal appears transparent to the eye. When imperfections develop in these crystals extra absorptions may appear in the visible region and the crystals will appear colored. One of the more interesting problems in solid state physics for many years has been the study of these imperfections in ionic crystals both experimentally and theoretically.

The color centers occurring in alkali halides come from many varieties of defects in the crystal. They occur when a few alkali or halogen ions are replaced by other ions or atoms, or when ions are removed, leaving ion vacancies in the crystal. There are also cases in which extra ions or atoms exist in the solids, forming interstitial impurities.

Distortions of the lattice from the perfect configuration of the crystal also can create color centers. In all cases, the effect of these color centers is to allow certain energy levels to exist in the gap between the conduction band and valence band of the energy band picture. Thus, energies needed to excite electrons from these color center levels to the allowed energy levels above are small compared to the energies of the interband transition or the energies from the valence band to the exciton levels. In some cases, this will happen in the visible light region, causing the crystal to appear colored, e.g., the F centers. In other cases, the excitation energies are outside the visible light region; thus, the crystal will remain transparent, e.g., the U centers.

2.2 Experimental Methods

Color centers are produced by many different kinds of techniques. They can be produced by exposing the crystals to X-rays or γ-rays, or by injecting electrons directly into the crystals. Bombarding the sample with heavy particles or electrons can also create imperfections in the solid. Another method is the process of additive coloration in which the crystal is heated in the presence of excess alkali or halogen or other atoms. Several review articles by Markham (1966) and Seitz (1946, 1954) have discussed these and other methods for producing color centers.

The optical absorption spectrum of a color center

generally shows a broad band whose position and shape are temperature dependent. For example, in the case of the F center, it is found that the width of the absorption band broadens with an increase of the temperature, while the peak energy of the band decreases with the increase of the temperature. It will be seen in section 2.4 that a very simple model for the F center can give a qualitatively good explanation for these characteristics of the absorption band.

A study of the peaks of the absorption bands in various alkali halides for a certain color center shows that there is a relationship between these energies and the nearest-neighbor distances of the solid. This kind of relation was first found empirically by Mollwo (1931) and later refined by Ivey (1947). In the cases of the U center and the F center, the relations are

$$E_{max} = \begin{cases} 20.16\ d^{-1.10} & \text{for U band} \\ 17.64\ d^{-1.84} & \text{for F band,} \end{cases} \qquad (2.1)$$

where E_{max} is in Electron Volts and d (the nearest-neighbor distance) is in Angstroms.

From the optical absorption data alone, very little information about the color center and its surroundings can be obtained. There are two other methods which can provide more insight into the structure of imperfections in the crystal. One of these methods is the Electron Spin Resonance method (ESR) (Hutchison, 1949) and the other is

the Electron Nuclear Double Resonance method (ENDOR) (Feher, 1957). These methods have been reviewed by Seidel and Wolf (1968) and Markham (1966).

In ESR spectroscopy, magnetic dipole transitions between the spin levels of an unpaired electron of the color center can be measured in a static magnetic field. In ENDOR spectroscopy, the nuclear spin resonances of the neighboring nuclei that are coupled to the unpaired electron of the color center are measured. Usually, these two resonance methods are applied only to the ground states of color centers. Measurements on excited states are difficult due to the short lifetime of these states.

From the ESR measurements, one can determine the nature of the center, that is, whether it is paramagnetic or diamagnetic. Sometimes the ESR absorption line is broadened due to the interactions between the magnetic moment of the unpaired electron and those of the neighboring nuclei, and information about the neighboring ions is difficult to obtain from the structureless absorption line shape. With the relatively new ENDOR measurements, more precise determination about the surroundings of the imperfection can be obtained and this provides an accurate way to check the ground state wave function of the paramagnetic center from theoretical calculations.

Using the data from these optical and magnetic measurements, models for these centers can be established and the

electronic structure of the color centers can be studied by various theoretical approaches.

2.3 Models for Color Centers

In the present calculations, only U, F, U_1, and U_2 centers in alkali halides are considered. From various experimental studies, especially ESR (Hutchison, 1949; Kip et al., 1953) and ENDOR (Feher, 1957; Seidel, 1961; Doyle, 1962), the F center can be established to be an electron trapped at an anion vacancy in the alkali halide crystal. The U center is believed to be a negative hydrogen ion substituted for an anion in the ionic crystal (Delbecq et al., 1956). The U_1 and U_2 centers are interstitial defects which occupy a position in-between the regular sites of the crystal. The U_1 center is believed to be a negative hydrogen ion at an interstitial position in the crystal and the U_2 center is a hydrogen atom at the same site (Delbecq et al., 1956; Spaeth, 1966).

The clusters of ions that are used in the present calculations for these color centers are shown in Figures 2.1-2.3.

Figure 2.1 shows the eight-center cluster (including the outer sphere) for the U center and the F center calculation with O_h symmetry. For the U center, it is a negative hydrogen ion in the center surrounded by six alkali ions. For the F center, the cluster is an electron trapped in the central sphere with six nearest alkali ions surrounding it.

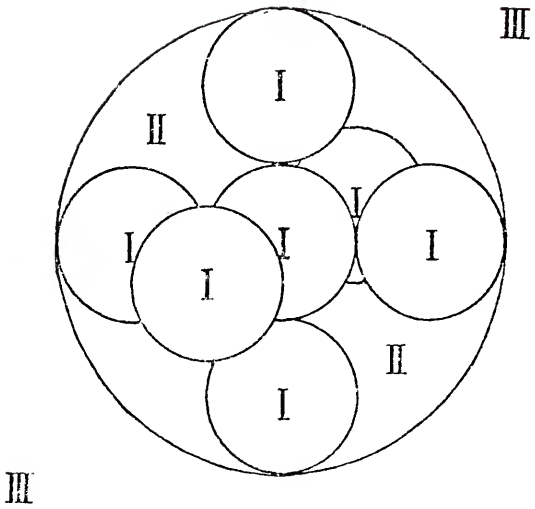

Figure 2.1. The eight-center cluster used in the calculation. Regions I, II and III are the atomic, intersphere and outer regions, respectively.

Figure 2.2 shows the cluster with T_d symmetry for the U_1 and U_2 center. In the case of the U_2 center, this cluster is a hydrogen atom in the center with four anions and four cations forming two interpenetrating tetrahedra. For the U_1 center, the central sphere is a negative hydrogen ion.

Figure 2.3 shows a large cluster with several shells of ions that is used in the U and F center calculations. This cluster has O_h symmetry, and the difference for the U center and the F center is at the central sphere which is occupied by a hydrogen ion in the case of the U center and an electron in the case of the F center. Calculations with the halogen ion in the central sphere of this cluster have also been done in order to compare with energy band calculations.

2.4 Theoretical Approaches

The F center is the simplest defect that can occur in alkali halides. As mentioned in the previous section, this center is an electron at the vacant anion site trapped in the potential well due to the near-by positive ions. An extremely simple model (Stockmann, 1952; van Doorn, 1962) in which the F center is thought to be a particle in an infinitely deep three-dimensional square well, i.e., a particle in a box, can qualitatively explain several properties of the optical absorption spectra that were mentioned before. Using this model, the excitation energy from the ground state to the first excited state is

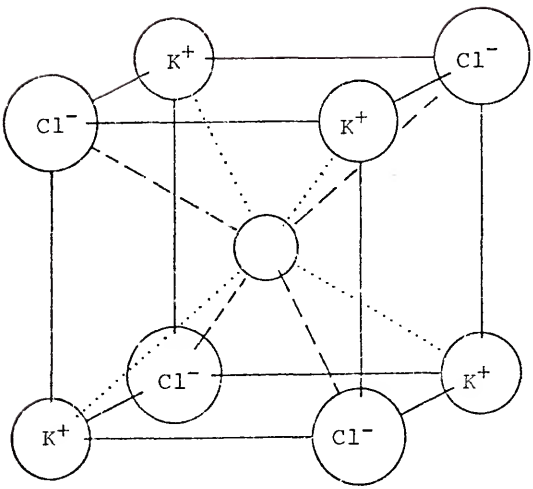

Figure 2.2. The cluster used in the U_1 and U_2 center calculations.

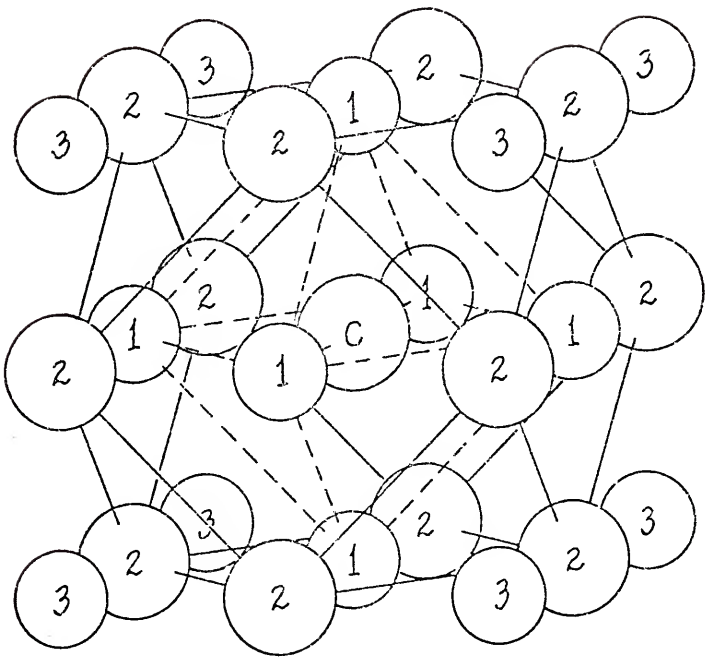

Figure 2.3. The large cluster with O_h symmetry used in the calculation. C=central ion, 1=first nearest-neighbor, 2=second nearest-neighbor, 3=third nearest-neighbor.

$$\Delta E = \left(\frac{3\pi^2\hbar^2}{8m} \right) d^{-2} \qquad (2.2)$$

where d is the distance from center of the potential well to the potential barrier. This relation shows the same form as the empirical relation for the F center in Equation (2.1). Thus, from this model the F band energy is found to be related directly to the spacing of the lattice. The decrease of the peak energy of the absorption band can be explained as the expansion of the lattice due to the increase of the temperature, and from the temperature dependence of lattice vibrations, the width of the absorption band can be expected to increase with the temperature.

Because of the simplicity of the electronic structure and the availability of the magnetic properties of an F center in an ionic crystal, this center served as a good testing example for the theoretical methods developed for the general impurity problem. Thus, most of the methods in the beginning are concentrated on the F center. Before 1957, the techniques used are mostly semi-empirical in nature. For example, there is a continuum model (Simpson, 1949) in which the polarizable crystalline medium is replaced by a dielectric continuum and the influence of lattice periodicity on the electron is considered by using an effective mass for the electron. A modified version, the semicontinuum model (Krumhansl and Schwartz, 1953), employs more detailed

treatment of potential for the central part of a color center in which the previous model fails. There are other methods using the variation techniques, e.g., the point-ion approximation (Gourary and Adrian, 1957) and molecular orbital calculation (Inui and Uemura, 1950). A summary of these methods up to 1960 is given by Gourary and Adrian (1960). More extensive calculations using the extended point-ion approximation (Wood and Joy, 1964) and pseudopotential approximation (Kubler and Friauf, 1965) have also been done. These methods are discussed in a review article by Fowler (1968). Since the U center has the same structure as the F center, calculations of U centers (Spector et al., 1967; Wood and Opik, 1967) have employed the same methods that were developed for the F center.

As to the U_1 center, there have been no theoretical calculations, partially because it has no interesting magnetic properties (the ground state is a closed shell) and partially because the peak of U_1 band in the absorption spectrum is generally not well defined (Delbecq et al., 1956; Rolfe, 1958). Contrary to the case of the U_1 center, a great deal of work has been done on the U_2 center. Kerkhoff, Martienssen and Sander (1963) examined various possibilities of the optical process for the U_2 center in a semi-classical way, and concluded that the optical U_2 band is due to a charge transfer from the nearest-neighbor halogen ions to the hydrogen atom. The configuration of the excited state of the U_2 center is thought to be a negative hydrogen ion

plus a hole in the p_π orbitals of the nearest-neighbor halogen ions. Using these configurations, Cho et al. (1966) and Cho (1967) obtain wave functions to discuss the hyperfine interaction.

Other calculations involving the variation technique have been done by Sammel (1969). Calculations of the transition energy of the U_2 band have been done semi-empirically by Hagston (1971) and Schechter (1969) and earlier by Mimura and Uemura (1959).

In this dissertation, the optical absorption energies of the U and F centers in alkali halides and the U_1 and U_2 centers in KCl are calculated. Unlike other approaches, the U centers, instead of the F centers, in various alkali halides were investigated first by using the multiple scattering method. This is because the starting potential used in the present calculation usually is a superimposed ion-potential and it is relatively simple to get an ion potential for the H^- ion by using the Herman-Skillman atomic program (Herman and Skillman, 1963).

In all calculations, the effects of the lattice distortion and polarization and the temperature dependence mentioned before are not included. Some of these effects, though, will be discussed in later sections. One of the purposes of the present calculation is to investigate the capability of the multiple scattering cluster method of handling the problem of impurities in solid; therefore, no adjustment of parameters to match the experimental data

was made. However, the effects of some of the parameters will be discussed in the results of the calculations given in Chapter 4.

CHAPTER III

METHODS OF CALCULATION

3.1 The Multiple Scattering Method

One practical way to solve the problem of a many-electron system is the one-electron self-consistent field method in which the interactions between the electrons and nuclei are replaced by the interactions of one electron with an averaged electronic charge distributions and with all nuclei plus some exchange-correlation effects. By solving the Schroedinger Equation in such a field, a set of eigenfunctions can be found and from these eigenfunctions the charge densities can be calculated. Thus, by repeating the procedures a self-consistent field can be reached. This method was first used by Hartree (1928) in his proposed one-electron equation.

If one starts from an anti-symmetrized one-electron product function or a Slater determinant function (Slater, 1929) to express the total energy of the system, a set of one-electron equations can be obtained by the variation technique. These are the Hartree-Fock equations (Fock, 1930) which have been used in many problems. For a complicated system, the exchange potential term in the Hartree-Fock equation becomes extremely difficult to calculate.

An approximate method called the $X\alpha$ method (Slater, 1972; Slater and Johnson, 1972) can be used to avoid the difficulty in the exchange-correlation potential. In this method, the exchange term in the Hartree-Fock one-electron equation is replaced by a local exchange potential (Slater and Wood, 1971) (see Equation (3.2)) which gives an approximate exchange-correlation term and is easy to calculate.

A numerical technique to solve the $X\alpha$ equation in a large molecule or cluster is the multiple scattering (MS-$X\alpha$) method (Johnson, 1973). In its formulation, the cluster is divided into three regions. The first is the atomic sphere region which contains one atom or ion inside the sphere. The second region is the intersphere region that is the space outside all the atomic spheres but inside an outer sphere which encloses the whole cluster. The third region is the outer region which includes all space outside the outer sphere. The problem is to solve the Schroedinger problem of a single electron in each region and after the matching of the wave functions and their first derivatives on all boundaries of the cluster we get a relation in which the eigenvalues can be determined. The one-electron wave function with spin up, $u_{i\uparrow}(1)$, satisfies the following $X\alpha$ equation (in Rydberg units).

$$\left[-\nabla_1^2 + V_c(1) + V_{X\alpha\uparrow}(1) + V_I \right] u_{i\uparrow}(1) = \varepsilon_{i\uparrow}\, u_{i\uparrow}(1) \quad (3.1)$$

where $V_c(1)$ is the Coulomb potential at position 1 due to all electronic and nuclear charges of the cluster, and $V_{x\alpha\uparrow}(1)$ is the statistical exchange-correlation potential which is given by

$$V_{x\alpha\uparrow}(1) = -6\alpha \left[\frac{3}{4\pi} \left(\sum_{i(\uparrow)} n_i u_i^*(1) u_i(1) \right) \right]^{\frac{1}{3}} \quad (3.2)$$

where the summation is over all eigenfunctions with spin up and n_i is the occupation number of the spin-orbital u_i. A discussion of the choice of α in this local exchange potential is given in the next section. The term V_I represents the Coulomb potential due to all ions outside the cluster. The determination of V_I is treated in section 3.5. Similar expressions of Equations (3.1) and (3.2) with spin down give the one-electron equation satisfied by $u_{i\downarrow}(1)$.

In order to simplify the problem, a muffin-tin form of potential has been used in the calculations. In this approximation, the potential inside the atomic sphere region is spherically averaged and the potential in the intersphere region is a constant equal to the volume average of potentials in that region. The potential in the outer region is also spherically averaged. Because of the locally spherically symmetric potential, we can express the solution of the one-electron Equation (3.1) in the αth sphere of the first region (for simplicity, the spin subscripts are

dropped for the following discussion) as

$$u^{\alpha} = \sum_{lm} C^{\alpha}_{lm} R^{\alpha}_{l}(|\vec{r}_{\alpha}|, \varepsilon) \, y_{lm}(\hat{r}_{\alpha}) \tag{3.3}$$

where $\vec{r}_{\alpha}$ is a vector measured from the center of the αth sphere and $y_{lm}(\hat{r}_{\alpha})$'s are the real spherical harmonics where $\hat{r}_{\alpha}$ represents the angular part of $\vec{r}_{\alpha}$, and C^{α}_{lm}'s are coefficients to be determined, and $R^{\alpha}_{l}(|\vec{r}_{\alpha}|, \varepsilon)$ is the solution of the one-electron radial Schroedinger equation with a certain energy ε, namely,

$$\left(-\frac{1}{r_{\alpha}^2} \frac{d}{dr_{\alpha}} r_{\alpha}^2 \frac{d}{dr_{\alpha}} + \frac{l(l+1)}{r_{\alpha}^2} + \bar{V}^{\alpha} - \varepsilon \right) R^{\alpha}_{l}(r_{\alpha}, \varepsilon) = 0$$

where $\bar{V}^{\alpha}$ is the spherically averaged potential in the αth sphere.

Similarly, the solution in the outer region can be written as

$$u^{o} = \sum_{lm} C^{o}_{lm} R^{o}_{l}(|\vec{r}_{o}|, \varepsilon) \, y_{lm}(\hat{r}_{o}) \tag{3.4}$$

where $\vec{r}_{o}$ is a vector measured from the center of the outer sphere. In the intersphere region, the volume average of V_C, V_X, and V_I gives a constant potential $\bar{V}_{II}$, and the solutions of the Schrcedinger equation for the cases $\varepsilon < \bar{V}_{II}$ can be expanded as

$$\begin{aligned} u^{II} = & \sum_{lm} A^{o}_{lm} \, i_{l}(Kr_{o}) \, y_{lm}(\hat{r}_{o}) \\ & + \sum_{\alpha} \sum_{lm} A^{\alpha}_{lm} \, k^{(1)}_{l}(Kr_{\alpha}) \, y_{lm}(\hat{r}_{\alpha}) \end{aligned} \tag{3.5}$$

where $K=(\bar{V}_{II}-\mathcal{E})^{\frac{1}{2}}$ and i_ℓ, $k_\ell^{(1)}$ are modified spherical Bessel and Hankel function, respectively. For the cases where $\mathcal{E} > \bar{V}_{II}$, the solution in the intersphere region can be expanded as

$$\mathcal{U}^{II} = \sum_{\ell m} A^{o}_{\ell m}\, i_\ell(Kr_o)\, Y_{\ell m}(\hat{r}_o) + \sum_{\alpha}\sum_{\ell m} A^{\alpha}_{\ell m}\, \eta_\ell(Kr_\alpha)\, Y_{\ell m}(\hat{r}_\alpha) \qquad (3.6)$$

where $K=(\mathcal{E}-\bar{V}_{II})^{\frac{1}{2}}$, and j_ℓ is an ordinary spherical Bessel function and η_ℓ is an ordinary spherical Neumann function.

In order to match the logarithmic derivative of the wave functions on the boundaries of a particular atomic sphere or the outer sphere, we have to transform the multi-centered wave function in region II in terms of only the one center that is under consideration. Several expansion theorems which are useful for this purpose have been discussed by Johnson (1973).

Suppose we consider the case of $\mathcal{E} < \bar{V}_{II}$ and try to match u^α and u^{II} (and their first derivatives) on the boundary of the th sphere. After cancelling the $C^{\alpha}_{\ell m}$ coefficients, we get a set of linear equations in terms of the $A^{\alpha}_{\ell m}$ coefficients, namely, for a particular ℓ and m

$$A^{\alpha}_{\ell m}\, t^{\alpha}_{\ell}(\mathcal{E})^{-1} + \sum_{\beta\neq\alpha}\sum_{LM} A^{\beta}_{LM}\, G^{\alpha\beta}_{\ell m, LM}(\mathcal{E}) + \sum_{LM} A^{o}_{LM}\, G^{\alpha o}_{\ell m, LM}(\mathcal{E}) = 0 \qquad (3.7)$$

where

$$t_{\ell}^{\alpha}(\varepsilon) = W\left[j_{\ell}(r),\ R_{\ell}^{\alpha}(r,\varepsilon)\right] \Big/ W\left[h_{\ell}(r),\ R_{\ell}^{\alpha}(r,\varepsilon)\right]$$

evaluated at $r = b_{\alpha}$ (the radius of the αth sphere). Here we have used the Wronskian bracket notation

$$W[x,y] \equiv x\frac{dy}{dr} - y\frac{dx}{dr}$$

. The $G^{\alpha\beta}_{\ell m, LM}(\varepsilon)$ coefficients depend only on the relative positions of centers in the cluster and are defined as

$$G^{\alpha\beta}_{\ell m, LM}(\varepsilon) = 4\pi\,(-1)^{\ell+L} \sum_{\ell' m'} i h^{(1)}_{\ell'}(K R_{\alpha\beta})\, Y_{\ell' m'}(\hat{R}_{\alpha\beta}) \times I_{\ell' m'}(\ell m; LM) \qquad \text{for } \varepsilon < \overline{V}_{I} \tag{3.8}$$

where $\vec{R}_{\alpha\beta}$ is a vector from the center of the αth sphere to the center of the βth sphere. The term $I_{\ell' m'}(\ell m; LM)$ is a Gaunt coefficient and is defined as an integral of the product of three spherical harmonics over all solid angles, namely,

$$I_{\ell' m'}(\ell m; LM) = \int Y_{\ell' m'}(\hat{r})\, Y_{\ell m}(\hat{r})\, Y_{LM}(\hat{r})\, d\hat{r} \tag{3.9}$$

Similarly,

$$G^{\alpha\alpha}_{\ell m, LM}(\varepsilon) = 4\pi (-1)^{\ell+L} \sum_{\ell' m'} i_{\ell'}(KR_{\alpha\alpha}) Y_{\ell' m'}(\hat{R}_{\alpha\alpha}) \times I_{\ell' m'}(\ell m; LM) \qquad \text{for } \varepsilon < \overline{V}_{II} \tag{3.10}$$

From above we know that in Equation (3.7) the dependence on the nature of a particular atom or ion in the cluster is only from the term $t^{\alpha}_{\ell}(\varepsilon)$ through its dependence on $R^{\alpha}_{\ell}(r_{\alpha}, \varepsilon)$, the solution of the radial Schroedinger equation, and the $G^{\alpha\beta}_{\ell m, LM}(\varepsilon)$ matrix element is only a structure factor with dependence on eigenvalue parameter ε through its relation with K.

After matching the logarithmic derivatives of the wave functions on the boundaries of all atomic spheres and the outer sphere, we complete the set of equations in terms of $A^{i}_{\ell m}$'s. It is well known that for such a set of homogeneous linear equations, the condition for having non-vanishing solutions for all variables requires that the determinant of the coefficients of these equations equals to zero. Thus,

$$\det \left\{ t^{i}_{\ell}(\varepsilon)^{-1} \delta_{ij} \delta_{\ell L} \delta_{mM} + (1-\delta_{ij}) G^{ij}_{\ell m, LM} \right\} = 0 \tag{3.11}$$

where the indices i and j start from the outer sphere and run through all atomic centers. The highest ℓ value used

in the calculation is dependent on the atoms and the symmetry of the cluster.

In the case that the cluster possesses symmetry, we can simplify the determinant by expanding the wave function in each region in terms of some linear combinations of the products of spherical harmonics and radial functions centered on the equivalent sites of the cluster that form bases for various irreducible representations of the appropriate symmetry group. The size of the symmetrized array of a particular representation that we need to solve is equal to the number of the basis functions that we used in that representation and is considerably smaller than that of (3.11) especially in the cases where the cluster has a high symmetry or many centers. In any case, the determinant can not be solved directly, but the zeroes of the determinant can be searched by evaluating the determinant in steps of the energy parameter $\mathcal{E}$.

For each eigenvalue $\mathcal{E}_i$ found, the eigenfunction in each region can be obtained. From these eigenfunctions, we can calculate the charge densities. After all eigenvalues $\mathcal{E}_i$'s are found, we can calculate the Coulomb potentials in each region by using the muffin-tin form of the total charge densities. Using the spherically averaged potential in region I and region III and the volume averaged potential in region II, the entire calculation can be started again.

In order to start the initial calculation, a super-

position of atomic potentials is used. For each new iteration, a weighted mixture of the newly generated potential and the previous one is used as the input potential. This procedure is repeated until the difference between the new and the old potentials is within a preset tolerance. Thus, self-consistency is achieved.

3.2 Choice of α in $V_{X\alpha}$

The statistical exchange-correlation potential (Slater and Wood, 1971) given in Equation (3.2) was originally derived by Slater (1951) with $\alpha = 1$, and later with another approach it was derived independently by Gaspar (1954) and by Kohn and Sham (1965) with $\alpha = 2/3$. In actual cases, values of α in between the above two values are expected to give better exchange-correlation effects. In the case of atoms, Schwarz (1972) has determined two sets of α's by using two different criteria. The first is to adjust the statistical total energy to the Hartree-Fock total energy of the isolated atom and the second is to adjust the parameter α so that the virial theorem is satisfied when $X\alpha$ orbitals are used in the RHF expressions for the expectation value of the kinetic and potential energies of the isolated atom.

The two sets of α's turn out to be very close to each other and the variation of α from atom to ion is not significant. Thus, it seems justified to use the same α for atom or ion in the solid. All of Schwarz' determinations were done without spin polarization. In the present calculations, the α_{HF} values with the Hartree-Fock total

energy criterion were used for all atomic spheres except for the hydrogen ion sphere in which the α value is equal to 0.77, which is appropriate for a spin-polarized calculation (Slater, 1973; Singh and Smith, 1971). For other ions, the α_{HF} values are approximately the same in a spin-polarized calculation. For the case of KCl, the same value of 0.72 was used both for the K^+ ion and the Cl^- ion. A weighted average of α is also used for the intersphere and the outer sphere regions. All the α values used for various ions in the present calculations and the α_{HF} and α_{VT} values determined by Schwarz (1972) are given in Table 3.1.

3.3 Transition State

In order to find the absorption energies of color centers in ionic crystals, the transition state concept (Slater, 1972) has been used in the multiple scattering Xα method.

Instead of calculating the difference of the total energies of the ground state and the excited state of the whole system, the excitation energy can be approximated by taking the difference of the one-electron eigenvalues of the two eigenstates involved in the transition with the occupation numbers set to be half-way between the initial and the final state of the system. In other words, one can remove one-half of the charge from the lower eigenstate and add one-half of a charge to the higher eigenstate to

TABLE 3.1

The α values used in the present calculations and the α_{HF} and α_{VT} values determined by Schwarz.

Ion	α	α_{HF}[a]	α_{VT}[a]
H^-	0.77000[b]		
Li^+	0.78147	0.78147	0.78087
F^-	0.73732	0.73732	0.73651
Na^+	0.73115	0.73115	0.73044
Cl^-	0.72000	0.72325	0.72277
K^+	0.72000	0.72117	0.72072

[a] Schwarz (1972).
[b] Singh and Smith (1971).

form a "transition state" of the system, and the excitation energy can be easily obtained from the eigenvalues.

The justification behind the transition state calculation follows from the fact that the eigenvalue in the $X\alpha$ method can be expressed as a first derivative of the total energy with respect to the occupation number of that state. Using the power expansion of the total energy, it can be shown that the error of the excitation energy for using the transition state calculation is mainly from the third order terms which can be shown to be relatively small (Slater and Wood, 1971).

3.4 Radii for Ions

In section 3.1, the division of space into three regions in the multiple scattering formulation has been discussed and the atomic region for each atom or ion is defined by a sphere. Thus, a set of radii acting as parameters for all atomic spheres is required in the calculation. Because of the muffin-tin approximation, it is natural to choose the radii of atomic sphere and outer sphere to touch one another so that the space in the intersphere region will not be too large, since the use of the constant potential in this region will probably contribute some errors to the final results.

For ionic crystals, there are a few sets of empirical ionic radii (Goldschmidt, 1926; Pauling, 1948) which are

widely used in many books. Thus, at the beginning of this investigation, several calculations were carried out by using the radii of Goldschmidt (1926) for the ion spheres. However, the basic reason for having such a set of radii is the fact that the differences between the values of the nearest-neighbor distance in the corresponding halides of a pair of alkali metals are approximately constant, and the same holds for the alkali metal salts of pairs of halogens; thus, by specifying any one radius, the whole set of ionic radii can be determined with a small correction so that the radii of anion and cation can add up exactly to the nearest-neighbor distance of that particular crystal. Different methods for choosing the radii generally will lead to a different set of ionic radii and a review of various kinds of ionic radii is given by Tosi (1965).

In order to make best use of the muffin-tin approximation, it is desirable to have a set of radii which are close to the relative sizes of ions in crystals. There are a few experiments employing the X-ray diffraction techniques to study the electron charge distributions of ionic crystal (Witte and Wolfel, 1955; Krug et al., 1955).

From the minimum of the charge densities in between a pair of anion and cation the crystal radii for this pair of ions can be defined. Using the above criterion, the crystal radii of the Na^+ and Cl^- ions are 1.17 Å and 1.64 Å, respectively. Starting from these two radii, Gourary and Adrian

(1960) were able to deduce a set of corrected radii for the ionic crystals. This set of radii give a larger relative size of cation to anion than that of the previous sets. Values of different sets of ionic radii mentioned are given in Table 3.2.

Calculations of various color centers by using Gourary and Adrian X-ray corrected ionic radii have been done for many alkali halides. The electronic charge in the intersphere region was observed to be less than those of previous calculations and the potential has a smaller discontinuity when we go from one atomic region to another. Therefore, in most of the calculations in this dissertation the corrected radii of Gourary and Adrian were used.

There are other ways to find the crystal radii for a particular ionic crystal, for example, by using the charge densities of ions or the potentials of the ions. But in most cases the radii determined are not far from the X-ray corrected radii.

Above all, the radii of the atomic spheres are not used as adjustable parameters in the present calculation. However, for some color centers, calculations with different sets of radii were available and effects of this variation of radii will be discussed in the results of those particular color centers.

TABLE 3.2

The ionic radii of Goldschmidt and the X-ray corrected radii of Gourary and Adrian.

Ion	Goldschmidt[a]		Gourary and Adrian[b]	
	(in A)	(in a.u.)	(in A)	(in a.u.)
Li^+ (LiF only)	0.78	1.47	0.92	1.74
Li^+	0.78	1.47	0.94	1.78
Na^+	0.98	1.85	1.17	2.21
K^+	1.33	2.51	1.49	2.82
F^- (LiF only)	1.33	2.51	1.09	2.06
F^-	1.33	2.51	1.16	2.19
Cl^-	1.81	3.42	1.64	3.10
Br^-	1.96	3.70	1.80	3.40

[a]Goldschmidt (1926).

[b]Gourary and Adrian (1960).

3.5 Ionic Correction Potential

In all of the present calculations except the U_2 center calculations, the cluster being used is not neutral. Thus, some form of the potential correction is needed to stabilize it. The most common method is by adding the potential from a charged sphere to the potential of the cluster. This method was first used by Watson (1958) to stabilize the $O^{=}$ ion. Using this technique with the charge on the Watson sphere being the negative of the charge Q of the cluster (see Table 3.3), the ionic correction potential V_I for an electron in Equation (3.1) is given by

$$V_I(r) = \begin{cases} \frac{2Q}{R} & \text{Ry} \quad \text{for } r \leq R \\ \frac{2Q}{r} & \text{Ry} \quad \text{for } r > R \end{cases} \tag{3.12}$$

where R is the radius of the Watson sphere, usually chosen to be the same as the outer sphere, and r is measured from the center of the cluster. With this charged sphere, the potential for the cluster will approach zero outside the cluster, and presumably the potential inside the cluster is close to the actual potential of the cluster imbedded in the solid. Several calculations were carried out with this potential correction, and some characteristics of this correction were found. That is, the correction inside the cluster depends on the choice of the radii of the ion spheres through the fact that the R in Equation (3.12) is always

TABLE 3.3

Constants in Equations (3.12) and (3.13) for various clusters used in the U center and F center calculations.

Cluster[a]	A	Q
Eight-center	3.96	5.00
Twenty-center	-3.97	-7.00
Twenty-eight-center	0.50	1.00

[a]See Figure 2.3. The eight-center cluster includes the first nearest-neighbors, and the twenty-center cluster includes the second nearest-neighbors, and the twenty-eight-center cluster includes the third nearest-neighbors.

equal to the sum of a constant (in the eight-center calculation, this constant is the nearest-neighbor distance) and the radius of the most distant ion of the cluster. The situation is more serious when the cluster has a large Q. A better potential correction, which depends only on the nearest-neighbor distance of the crystal, is needed. There are several methods for calculating the Madelung potential inside the ionic crystal (for a review, see Tosi (1965)), and for the present purpose the Evjen method (Evjen, 1932) is a simple method which can be easily programed to use in a computer. A volume average of the potential due to the surrounding ions is calculated inside the cluster and details of this calculation are discussed in Appendix A. Thus, the ionic correction potential for an electron can be rewritten as

$$V_I(r) = \begin{cases} \frac{2A}{d} \quad \text{Ry} & \text{for } r \leqslant R \\ \frac{2Q}{r} \quad \text{Ry} & \text{for } r > R \end{cases} \tag{3.13}$$

where d is the nearest-neighbor distance or the anion-cation distance in an ionic crystal, A is a constant, which depends on the size and structure of the cluster. The different values of A for various clusters are given in Table 3.3.

In a large cluster, the volume averaged correction potential is not sufficient to give a reasonable correction

for each ion, therefore, separate ionic correction potentials for ions were sought. Since the potential for each ion in the muffin-tin approximation is spherically averaged, the correction potential for each ion is particularly simple to find.

We note that in the jth ion sphere of the cluster the ionic correction potential at an arbitrary point, $\vec{r}_j$, is given by

$$V_I(r_j) = - \sum_i \frac{2q_i}{|r_j - R_{ji}|} \quad R_y \qquad (3.14)$$

where $\vec{r}_j$ is measured from the center of the jth sphere, the summation of i is over all ions outside the cluster and q_i is the point charge of ith ion, and $\vec{R}_{ji}$ is a vector measured from the center of the jth sphere to the ith ion. It can be shown very easily that the spherically averaged $V_I(\vec{r}_j)$ is equal to the ionic correction potential at the center of the jth sphere:

$$\frac{1}{4\pi} \iint V_I(\vec{r}_j) \sin\theta_j \, d\theta_j \, d\varphi_j = - \sum_i \frac{2q_i}{R_{ji}} \quad R_y \qquad (3.15)$$

Therefore, the ionic correction potential for an electron inside any ionic sphere is a constant and can be calculated by using the Madelung constant α_M (see Appendix A), e.g.,

$$\bar{V}_I(j) = -\sum_i \frac{2q_i}{R_{ji}} = -\frac{2\alpha_M}{d} + \sum_{k\neq j} \frac{2q_k}{R_{jk}} \equiv \frac{2A_j}{d} \quad Ry, \tag{3.16}$$

where d is the nearest-neighbor distance of the crystal, the summation of k is over all ions in the cluster except the jth, and R_{jk} is the distance from the jth center to the kth center. The ionic correction potential in the intersphere region of the cluster can also be found by the following method. The spherically averaged or the volume averaged potential inside the outer sphere of a cluster due to all ions outside will give a constant potential that is the same as the potential at the origin of the cluster, and since the potentials inside the ion spheres are known, the ionic correction potential for the intersphere region can be calculated from the following equation:

$$\bar{V}_I(\text{int}) = \frac{V_I(0)\cdot S_o - \sum_k \bar{V}_I(k)\cdot S_k}{S_o - \sum_k S_k} \equiv \frac{2A_{\text{int}}}{d} \quad Ry, \tag{3.17}$$

where $V_I(0)$ is the potential at the center of the cluster, S_o is the volume of the outer sphere, the summation of k is over all the ion spheres in the cluster, and S_k is the volume of the kth ion sphere. The value of A_{int} depends

on the relative size of the cation and anion, and values of A_{int} for KCl and LiF along with the A_j's for the large cluster shown in Figure 2.3 are given in Table 3.4. The correction potentials for the outer region in all cases are the same as defined in Equation (3.12).

TABLE 3.4

Constants in the separate ionic correction potentials for the twenty-eight-center cluster.

Region	A_j or A_{int}[a]
Central ion sphere	0.386
First nearest-neighbor	0.439
Second nearest-neighbor	0.235
Third nearest-neighbor	0.682
Intersphere (KCl)	0.381
Intersphere (LiF)	0.477

[a]The twenty-eight-center cluster is shown in Figure 2.3. Constants are defined in Equations (3.16) and (3.17).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The U Centers in Alkali Halides

The peak energies of the optical absorption band of the U centers in several alkali halides have been calculated with the use of the eight-center cluster (see Figure 2.1), which has been discussed in section 2.3. The electronic structure and the absorption energy of the U center in KCl have also been calculated using the twenty-center cluster. This has a negative hydrogen ion at its center and includes up to the second nearest-neighbors. Calculations with the twenty-eight-center cluster shown in Figure 2.3 including up to the third nearest-neighbors have also been done.

All calculations have been carried out using the spin-polarized multiple scattering Xα method in which a separate local exchange potential for each spin is used in the one-electron equation. The α values used for the various atomic regions are given in Table 3.1. In the U center calculation, the α value for the hydrogen sphere is 0.77 which is usually used in a spin-polarized calculation of a two-electron ion (Slater, 1973; Singh and Smith, 1971).

The input data for the U center calculations using the eight-center cluster are given in Table 4.1. The interionic

TABLE 4.1

Radii used in the eight-center cluster calculations of the U centers and the F centers in alkali halides.

Crystal	d^a	R_+	R_-	R_{out}
LiF	3.800	1.740	2.060	5.540
NaF	4.370	2.190	2.180	6.560
NaCl	5.310	2.210	3.100	7.520
NaBr	5.630	2.210	3.420	7.840
KF	5.046	2.834	2.212	7.880
KCl	5.934	2.834	3.100	8.768
KBr	6.220	2.820	3.400	9.040

All quantities are measured in atomic units.
[a]Tosi (1965).

distance (d), shown in the first column, is the same as the equilibrium nearest-neighbor distances in a pure crystal. The R_+'s are the radii for the alkali spheres and the R_-'s are the radii for the halogen spheres, which is occupied by a negative hydrogen ion in the present case. All radii are chosen according to Gourary and Adrian's corrected ionic radii (shown in Table 3.1), although small adjustments were made so that the atomic spheres touch one another. R_{out} is the radius of the outer sphere. The averaged Madelung potential correction defined in Equation (3.13) was used for all these calculations.

The electronic structure of the ground state of the U center in KCl calculated by using the eight-center cluster is shown in Figure 4.1. In this diagram, one can see that no spin-polarization effect appeared in the eigenvalues. This is expected from a system consisting of closed shell ions. The hydrogen 1s level appears as two a_{1g} symmetry orbitals, one with each spin. These two hydrogen a_{1g} levels are well localized in the central part of the cluster as the calculated result showed that 85% of the charge of these levels is within the central sphere and the rest of the charge is distributed mostly in the intersphere region.

Below the hydrogen levels, the next occupied levels are a group of seven levels for each spin that arise from the atomic 3p levels of the six K^+ ions. These levels are relatively deep compared to the hydrogen a_{1g} orbital and

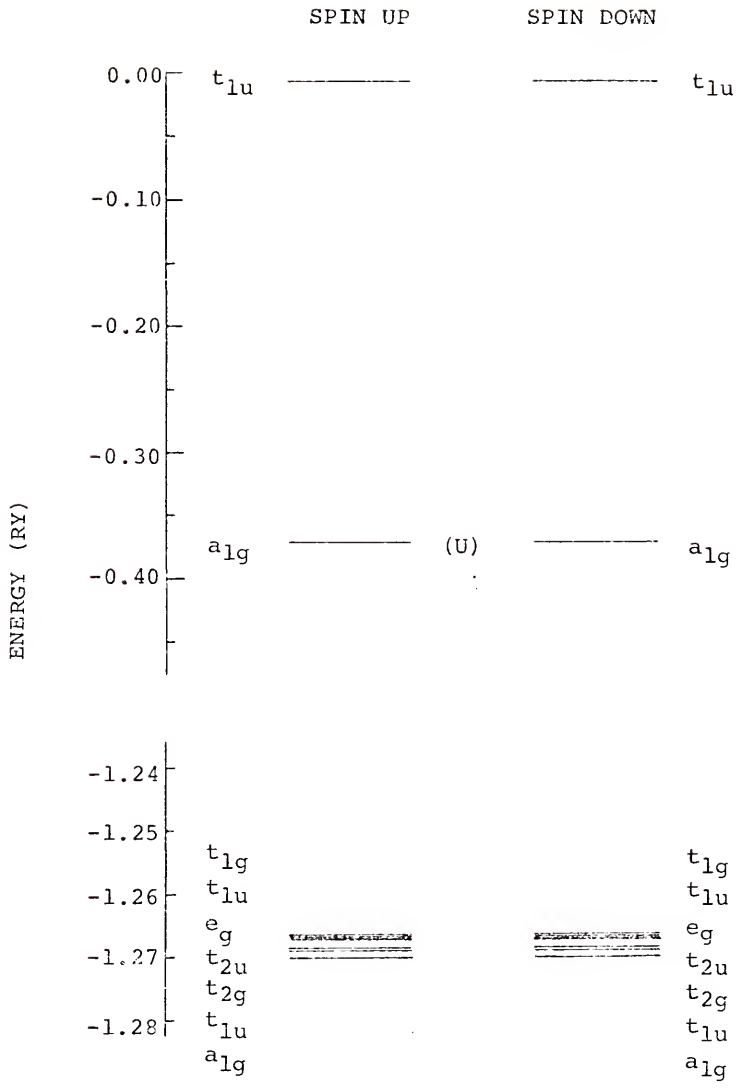

Figure 4.1. The ground state electronic structure of the U center in KCl calculated by using the eight-center cluster.

their charge distribution is concentrated in the six K^+ spheres. Hence, only a small interaction is expected between this group of levels and the hydrogen levels. The excitation of the U center in this picture is expected to be an electron excited from the hydrogen a_{1g} orbital to the next higher allowed level, which is a t_{1u} symmetry orbital with the same spin. By using the transition state concept discussed before, the excitation energy for the U center can be calculated.

The calculated transition energies of the U center for several alkali halides are shown in Table 4.2 along with the experimental absorption energies and other theoretical results. The $\varepsilon(a_{1g})$ and $\varepsilon(t_{1u})$ are the eigenvalues of the two states involved in the excitation process in a "transition state" calculation, and the difference of these two energies gives the present value, ΔE, for the U center absorption. Comparing with the experimental results, one can see that ΔE's are in good agreement with the observed values, especially for the two potassium halides. Two other sets of energies are also given in Table 4.2. One of them is calculated by Gourary and Adrian (1957) and Spector et al. (1967) using the point-ion model and their values are given under ΔE_{pi}, and the other set of values, ΔE_{Ivey}, is calculated by Ivey's relation given in Equation (2.1), which is determined empirically from the experimental data.

The absorption energies obtained both theoretically and

TABLE 4.2

The optical absorption energies of the U centers in alkali halides calculated by using the eight-center cluster.

Crystal	d	$\varepsilon(a_{1g})$	$\varepsilon(t_{1u})$	ΔE	ΔE_{exp}[a]	ΔE_{PI}[b]	ΔE_{Ivey}[c]
LiF	3.800	-0.646	-0.069	0.577		0.596	0.687
NaF	4.370	-0.569	-0.059	0.510		0.506	0.588
NaCl	5.310	-0.523	-0.082	0.441	0.475	0.406	0.475
NaBr	5.630	-0.502	-0.092	0.410	0.434	0.378	0.446
KF	5.046	-0.515	-0.050	0.465		0.432	0.503
KCl	5.934	-0.488	-0.061	0.427	0.426	0.356	0.421
KBr	6.220	-0.472	-0.068	0.404	0.400	0.338	0.400

All energies are in Rydberg and distances are in atomic units.
[a]Schulman and Compton (1962).
[b]Gourary and Adrian (1957), Spector et al. (1967).
[c]See Equation (2.1).

experimentally are plotted against the nearest-neighbor distances of alkali halides in Figure 4.2. As one can see from this figure, Ivey's relation is the result of averaging experimental data, and there is in fact considerable deviation from it.

The absorption energies calculated by the point-ion model show a smooth curve in parallel with the Ivey's empirical curve, and their values can be fitted to a relation with the same form as the Ivey's. Unfortunately, this simple model produces results which are approximately 15% lower than the observed values. In the point-ion model calculation of the U center, one uses a trial wave function for a ground state, with variation parameters to be determined, in a field produced by all surrounding ions which are treated as point charges. By minimizing the energy expression of the Hamiltonian for this two-electron system using the trial wave function, one can obtain the energy for the ground state. A similar procedure using another trial wave function gives the energy of the excited state, thus, the excitation energy of the U center can be found. In this point-ion model, only the nearest-neighbor distance of the crystal is directly involved in the calculation, it is not surprising that the calculated energy changes smoothly with the interionic distance of the crystal. On the contrary, the results calculated from the present cluster method do show some deviations from the smooth

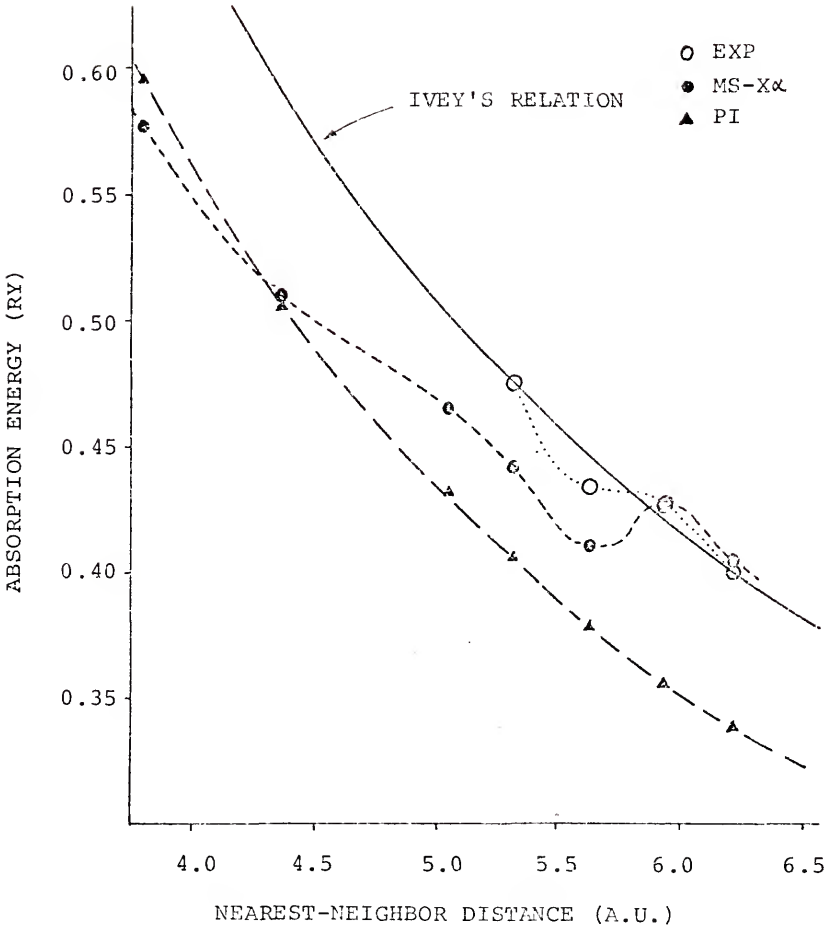

Figure 4.2. The optical absorption energies of the U center as a function of the nearest-neighbor distance of the crystal.

variation of an Ivey type of relation. This can be seen, especially for the case of the NaBr crystal with an interionic distance of 5.63 a.u., in Figure 4.2. In that case, the U center energy is lower than the energy for a U center in KCl which has an interionic distance of 5.934 a.u. As one can see, the experimental results also indicate the same characteristics in that region. Therefore, the present model, including the detailed structure of the first nearest-neighbors, does show that although the interactions between the hydrogen ion and the six alkali ions are expected to be small as discussed before, the effects on the energy levels and wave function of the U center due to the structure of the surrounding alkali ions are, nevertheless, not negligible. Wood and Opik (1967) have also calculated the U center absorption energies in potassium halides by a semi-empirical method. In their calculation, the electronic structure of the first nearest-neighbor ions is considered, and the calculated transition energies, 0.409 Rydbergs in KCl and 0.403 Rydbergs in KBr, showed an energy somewhat too low for KCl and a comparable energy for the KBr case. They also tried another calculation by including polarization effects and taking more surrounding ions into consideration and obtained a transition energy of 0.437 Rydbergs for KCl which is higher than the experimental value by approximately the same amount as the difference of their first calculated result. In any case, the ability of a model to predict a

single transition energy is not a very satisfactory criterion for the validity of the model. It is necessary at least to examine several cases to obtain a better understanding of the model that is used. Thus, the calculation of Wood and Opik and the calculation of Hayns (1972), in which only the U center transition energy in LiF was calculated by a semi-empirical CNDO method, will not be discussed.

Experimental data for the U center absorption energy are available for several alkali halides with interionic distance greater than and equal to that of the sodium chloride crystal. Comparison of the present calculated energies with the observed values shows that the average deviation is about 3.5%, which is very good. For alkali halides, with interionic distances less than that of the sodium chloride crystal, one has to consider that the results from Ivey's empirical relation will probably give a reasonable guess as to the transition energy of the U center. From Figure 4.2, the results from the present cluster method can be seen to deviate away from the predictions of the Ivey relation as the nearest-neighbor distance gets smaller.

For the case of the LiF crystal, which has the smallest interionic distance of 3.8 a.u., the transition energy calculated is 0.577 Ry which is approximately 16% lower than Ivey's result and is comparable to the calculated value of the point-ion model. Discussion of the possible causes for this drop in the calculated U center excitation energy in the region of small interionic distance and of the

neglected factors, namely, the lattice distortion and polarization effect, will be given later.

At first, it may seem that the resulting curve of the cluster model in Figure 4.2 is quite complicated as to its variation with the interionic distance despite the fact that it has been shown to be consistent with the experimental data. With a closer examination, the calculated energies do show a characteristic variation with the interionic distance within the sodium halides and the potassium halides (see Figure 4.3). This is reasonable, since in the eight-center calculation only the nearest cations are considered directly in the calculation and the variation within a certain family of cation only changes the space occupied by the H^- ion. Therefore, the difference in energy between the ground state and the excited state of the U center decreases with the increase of the space occupied by the H^- ion, but for the same space occupied by H^- ion with a different set of cations, the lighter cations will give a larger difference between the two levels of the U center. In the point-ion calculation, the effect of the nearest cation is only related to the distance measured from the center of the cation, since only the Coulomb potential of point-charge of that cation is considered. Thus, the interionic distance, which is the sum of the size of H^- and that of the nearest cation, will be related directly to the U center transition energies. On the other hand, the effects of cations are shown in the cluster calculation. This implies that the

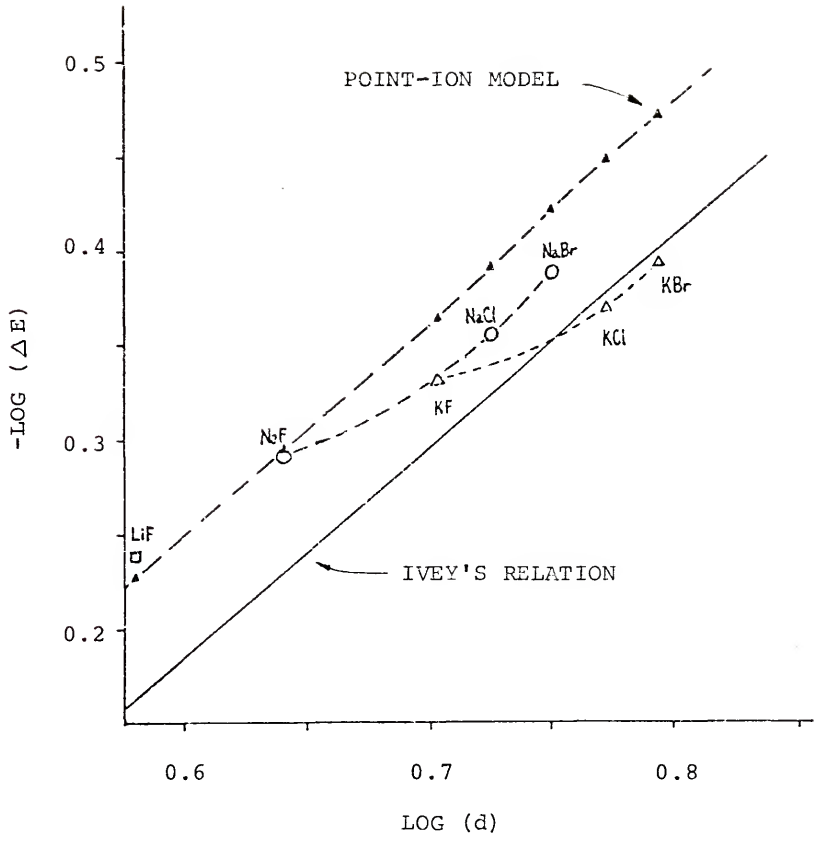

Figure 4.3. The logarithmic graph of the optical absorption energies of the U center, ΔE (in Ry), as a function of the nearest-neighbor distance of the crystal, d (in a.u.).

interactions between the hydrogen ion and different cations have different degrees of deviation from the interactions between a hydrogen ion and the approximated point-charges of the cations. We can see in Figure 4.3 that the transition energies calculated from the cluster for the sodium halides and the potassium halides fall on different curves. The reason for this is probably the different ionicities of the sodium ion and the potassium ion. In other words, the electronic charge distributions of different cations have slightly different forms, a feature which cannot be included in the point-ion model.

In order to investigate this possible difference, the electronic charge distribution within each region in the transition state cluster calculation for various alkali halides is shown in Table 4.3. Now, the transition state is, in the exact case, a mixed state corresponding to equal weighting of single determinant ground and excited states (Trickey, 1973). Comparing the charge distribution of the ground state to that of the transition state in KCl, one finds that the charge inside the K^+ sphere, Q_+, almost stays the same (difference is less than 0.001 e), and a fraction of an electronic charge (about 0.32 e) is transferred from the hydrogen sphere to both the intersphere region and the outer region as the cluster goes from the ground state to the transition state. With this in mind, one can use the general features of the charge distributions given in Table 4.3 to discuss the problem mentioned above.

TABLE 4.3

The distribution of electronic charges within each region in the U center transition state calculation.

Crystal	Q_+	Q_{H^-}	Q_{int}	Q_{out}
KBr	17.842	1.450	1.274	0.224
KCl	17.846	1.410	1.242	0.271
KF	17.849	1.260	1.187	0.455
NaBr	9.954	1.455	0.681	0.143
NaCl	9.954	1.408	0.682	0.187
NaF	9.954	1.239	0.659	0.380
LiF	1.998	1.201	0.442	0.369

All calculations are carried out using the eight-center cluster.

From Table 4.3, one finds that the charges in the K^+, Na^+, and Li^+ ion spheres are approximately 17.85, 9.95, and 2.00 electron charges, respectively, thus, the net charges inside the K^+, Na^+, and Li^+ ion spheres are approximately +1.15, +1.05, and +1.00, respectively. The electronic charges of cations outside the ion sphere are mostly in the intersphere region, and the Coulomb potential due to this diffused charge of the cations in the hydrogen sphere is smaller than the Coulomb potential with all these charges in the cation spheres. Therefore, the net Coulomb effect of a potassium ion gives an equivalent charge of more than +1. The sodium ion also has an effective ionicity greater than +1 but less than that of the potassium ion. The lithium ion has an ionicity equal to +1. Since the a_{1g} orbital of the U center is localized in the central part of the cluster as one can see from the general features of the charge distribution of this orbital given in Table 4.4, the energy of this a_{1g} orbital is expected to be lower than that in a point-ion field, and the amount of this difference for the potassium halides is larger than that of the sodium halides. On the other hand, the charge distribution of the excited state (the t_{1u} orbital) of the U center is mainly in the intersphere region and the outer region (see Table 4.4). Since in general there is more charge in the intersphere region for the potassium halides than for the sodium halides, the energy of this t_{1u} orbital is expected to have a higher

TABLE 4.4

The charge distribution of the ground state and the excited state orbitals of the U center in a transition state calculation.

Orbital	Crystal	Q_{H^-}	Q_+	Q_{int}	Q_{out}
	KBr	0.891	0.004	0.085	0.001
	KCl	0.872	0.005	0.096	0.001
	KF	0.775	0.014	0.142	0.001
a_{1g}	NaBr	0.883	0.003	0.099	0.000
	NaCl	0.864	0.004	0.113	0.000
	NaF	0.774	0.009	0.169	0.001
	LiF	0.754	0.009	0.191	0.001
	KBr	0.059	0.013	0.506	0.360
	KCl	0.032	0.012	0.432	0.465
	KF	0.002	0.006	0.163	0.801
t_{1u}	NaBr	0.119	0.013	0.541	0.263
	NaCl	0.077	0.013	0.497	0.349
	NaF	0.007	0.008	0.223	0.723
	LiF	0.011	0.006	0.226	0.725

energy in the case of the potassium ions surrounding a H^- ion than in the case with sodium ions surrounding a H^- ion. Therefore, the U center transition energies for potassium halides will be generally higher than those of the sodium halides. Precisely this sort of behavior is exhibited in Figure 4.3. Of course, one should not compare the U center transition energies between these two families of alkali halides quite so directly. For example, in the cases of NaCl and KCl, the small interionic distance of NaCl is still the dominating factor which makes the transition energy in NaCl greater than that in KCl. On the other hand, the argument given above does explain the cause of the calculated U center energy in NaBr being smaller than that in KCl.

Another result is that there is a larger difference between the calculated energy and Ivey's result in an alkali fluoride than the corresponding differences in an alkali chloride and an alkali bromide (see Figure 4.3). This suggests that the relatively small size of the F^- ion has a strong effect on the hydrogen ion. As shown in Table 4.4, the charge distribution of the ground state of the U center inside the central hydrogen sphere for an alkali fluoride is less than that of the corresponding alkali chloride or alkali bromide and the charge in the intersphere region is increased in the case of an alkali fluoride. Thus, the energy of this state is expected to have an additional shift upward as compared to the other cases. For the U center excited

state in an alkali fluoride, the charge distribution is mostly in the outer region, thus, this is a very extensive orbital as compared to the other cases. A more accurate representation of this state probably needs the consideration of more neighbors into the calculation or other semi-empirical methods, but the energy of this state is believed to be not far from the present value. There are no experimental data on the U center energies for the alkali fluorides. Thus, the present calculated values cannot be evaluated directly. Nevertheless, U center calculations in various alkali halides which use the small cluster multiple scattering calculation give a good description of the electronic structure and the absorption energies. The absorption energies calculated for KCl and KBr are in excellent agreement with the observed values, although this agreement is probably somewhat coincidental since some effects were neglected in the calculations and the effects of the parameters and approximations used in the calculation should be considered.

The most common effects discussed in the color center calculation are lattice distortion and polarization. To incorporate the lattice distortion into the present calculation is relatively simple. A preliminary result showed that the U center transition energy is increased if the neighboring ions are allowed to displace inward, and in fact, an estimate can be obtained directly by using the graph shown in Figure 4.3. At present, the determination of the amount of the

lattice distortion near the U center by fitting data to the experimental results is certainly unwarranted since there are other effects to be considered. Thus, no attempt was made in this regard, though a rough estimate showed that the U center transition energy in KCl will increase about 0.004 Ry if the first nearest-neighbor ions are allowed to displace inward by 1% of the interionic distance of the crystal. Furthermore, in the excited state the probability for finding the electron outside the first nearest-neighbor distance from the center will be appreciable. Thus, the lattice distortion effect is expected to be more important in the excited state than the ground state of the U center. Nevertheless, the lattice distortion caused by the U center is certainly smaller than the distortion caused by the F center, and one calculation (Wood and Joy, 1964) estimated the distortion of the ground state of the F center is of the order of 1% or less.

When an electron moves out of the vicinity of the color center, the surroundings of the electron will be polarized, and this polarization will follow the movement of the electron. Gourary and Adrian (1960) have discussed the quasi-adiabatic approximation to consider the instantaneous field at the position of the electron. But there are many difficulties in this approximation. For the one-electron self-consistent field method, each electron is supposed to respond only to the averaged positions of all other electrons.

Thus, the polarization effect cannot be considered in the present calculation. For the ground state of the U center, the electron will stay mainly in the central region and the polarization effect will be negligible. For the excited state, the polarization effect probably will lower the energy of this state, but the effect is expected to be small.

As to the effects of the approximations and parameters used in the present calculation, the muffin-tin approximation is expected to be a good approximation, since the X-ray diffraction experiment (Witte and Wolfel, 1955) for NaCl showed that the charge distribution is nearly spherical for the ions and only a very small amount of charge is in-between the ions. The gradient of the charge densities in this interion region is small. For the case of LiF (Krug et al., 1955), the charge distribution is less spherical near the outer part of the ions as compared to the case of NaCl. It is thought in this case the anions are relatively soft, so that some overlapping of charge densities from different ions can occur. One of the problems of using this approximation usually comes from the uncertainty in choosing the radii for the atomic spheres. From the treatment of the intersphere potential as a constant, one knows that an appropriate choice of radius for each ion is certainly essential. In section 3.4, the choice of the radii for the ions has been discussed, and the X-ray corrected radii of

Gourary and Adrian (X.R.) are used for all the calculations. In order to see the effects for using different sets of radii, a U center calculation in KCl with the ordinary ionic radii of Goldschmidt (O.R.) was carried out. The results of these two transition state calculations in KCl are shown in Table 4.5. In the O.R. case, the size of the K^+ ion is decreased as compared to the size in the X.R. case, and this decrease is the direct cause for the drop in electron charge inside the K^+ sphere. Thus, the net charge inside the K^+ sphere is about +1.32 which is higher than the net charge (about +1.15) in the X.R. case. Similarly, the charge inside the H^- sphere is increased due to the increase of the size of the hydrogen sphere. The major effects of using the O.R. as compared to the X.R. are the increase of the electronic charge in the intersphere region and the decrease in energies of the ground state and the excited state of the U center, and also a decrease of the U center transition energy. The increase of the charge in the intersphere region indicates that the O.R. gives a worse representation for the size of the ions in crystal than the X.R. does. The more positive charge of the K^+ sphere in the O.R. case gives a deeper potential for the hydrogen ion, consequently, the energy levels of the U center are lowered. The transition energy of the U center is lowered by 0.01 Ry in the O.R. case which is about 2.5% of the energy.

So far all the calculations have used the ionic

TABLE 4.5

Comparison of the U center transition state calculations in KCl with two different sets of ionic sphere radii.

	X.R.[a]	O.R.[b]
$V_I(r \leq R_{out})$[c]	1.335	1.335
R_{out}	8.768	8.448
R_-	3.100	3.420
R_+	2.834	2.514
ΔE	0.427	0.417
$\varepsilon(a_{1g})$	-0.488	-0.497
$\varepsilon(t_{1u})$	-0.061	-0.080
Q_{out}	0.270	0.255
Q_{int}	1.240	2.157
Q_{H^-}	1.410	1.509
Q_{K^+}	17.846	17.680

All energies are in Rydbergs and distances are in a. u.
[a]Radii of Gourary and Adrian (1960).
[b]Radii of Goldschmidt (1926).
[c]Calculated from Equation (3.13).

correction potential defined in Equation (3.13). Several calculations with the Watson sphere correction (see Equation (3.12)) are shown in Table 4.6. In this table two sets of radii are used in both the KCl and the LiF calculations. Comparing the charge distribution of the cluster in KCl with two different kinds of radii, one finds essentially the same differences that are found in the calculations with the averaged correction potential (see Table 4.5). With the Watson sphere in the calculation, the potential inside the cluster is lower than that with the averaged correction potential in these calculations. This shifts the energy levels of the U center down and a small fraction of the charge redistributes from the outer region to the inside of the cluster. The charges inside the cation spheres stay the same. Comparing the transition energies found for different ionic correction potentials, one finds that these energies vary due to the relative insensitivity of the U center excited state as compared to the ground state. Thus, the correction potential for a cluster embedded in the solid is essential in finding an accurate optical absorption energy in the U center. Further, as can be seen in Table 4.6 the differences in the transition energies between calculations which use the X.R. and the O.R. are 0.02 Ry and 0.04 Ry in the cases of KCl and LiF, respectively. The difference for the case of KCl is doubled as compared to that of the previous calculations shown in Table 4.5. One important

TABLE 4.6

Comparison of the U center calculations with different sets of radii using the Watson sphere potential correction.

	KCl		LiF	
	(O.R.)	(X.R.)	(O.R.)	(X.R.)
$V_I(r \quad R_{out})$	1.184	1.141	1.965	1.805
R_{out}	8.448	8.768	5.090	5.540
R_+	2.514	2.834	1.290	1.740
R_-	3.420	3.100	2.510	2.060
ΔE	0.438	0.458	0.624	0.662
$\varepsilon(a_{1g})$	-0.628	-0.653	-0.766	-0.865
$\varepsilon(t_{1u})$	-0.190	-0.195	-0.142	-0.203
Q_{out}	0.138	0.091	0.174	0.104
Q_{int}	2.200	1.350	0.860	0.652
Q_{H^-}	1.540	1.439	1.380	1.217
Q_+	17.680	17.850	1.928	2.004

All energies are in Rydbergs and distances are in atomic units. O.R.=ionic radii of Goldschmidt (1926). X.R.= X-ray corrected radii of Gourary and Adrian (1960).

factor for causing these differences is the dependence of the Watson sphere potential on R_{out} for the cluster (see section 3.5). Therefore, the averaged correction potential of Equation (3.13) is a better potential to use in the present eight-center cluster calculations.

For most of the calculations in various alkali halides, the X-ray corrected radii give fairly good results for the transition energies, and the potential calculated has a smaller discontinuity in crossing the boundary of the neighboring ionic spheres than is the case when the ordinary ionic radii are used. Exceptions are the cases of the alkali fluorides, namely, KF and NaF. In these cases, preliminary results show that the transition energies calculated by using O.R. are somewhat higher than the previous results and closer to Ivey's results. Above all, the variations of the results due to different sizes of the ions are relatively small, as one can see in the case of KCl, for which the variation is only 2.5%.

Actually, any set of ionic radii is only an approximation to the apparent sizes of the ions in crystals. Thus, in order to get a more accurate result on the sizes of ions in each crystal, one needs to find them separately by using the criteria of charge densities or potentials. Eventually, the removal of the muffin-tin restriction on the potential can eliminate the necessity of choosing radii for the ion spheres and the error introduced by this approximation.

In all calculations, the parameter α in the local exchange potential for each region is not varied. The detailed effects of choices of α have not been investigated, but in general a higher α value will give the electron a deeper potential. Thus, an α value greater than 0.77 in the hydrogen sphere will probably lower the states of the U center and will probably result in a slightly higher transition energy for the U center.

Several effects associated with the present cluster calculation have been discussed and most of these effects are small. From Figure 4.2, the calculated energies can be seen to deviate from Ivey's relation in the region of small interionic distance. One possible cause is the assumption of the point charges for the surrounding ions in calculating the average correction potential. This may become improper as the interionic distance gets too small. There are no experimental results on a U center in the region of small interionic distances. A similar problem will be discussed later, in the section on F center calculations.

A calculation on the U center in KCl using the twenty-center cluster (including the outer sphere) has also been carried out. In this cluster the central hydrogen ion is surrounded by six K^+ ions and twelve Cl^- ions. The radii of the atomic spheres are the same as those used in the eight-center cluster calculation. The α values used in various regions are given in Table 3.1. At first, the correction

potential used in the calculation is chosen simply to be an average of the ionic correction potentials at the centers of all atomic spheres which can be calculated by using Equation (3.16). This constant correction potential for an electron inside the cluster equals to -8.32/d Ry, where d is the nearest-neighbor distance of the crystal. From the transition state calculation the U center absorption energy is found to be 0.34 Ry which is about 20% lower than the observed value.

Another calculation has used the averaged correction potential defined in Equation (3.13). This correction potential for an electron inside the cluster equals -7.94/d Ry which is higher than the previous potential by 0.067 Ry. The results of the transition state calculation show no significant change from the previous calculation. The calculated U center absorption energy is equal to 0.32 Ry. The charge in the intersphere region has 10.12 electronic charges which is very large compared to that of an eight-center cluster calculation. This is mainly from the fact that only 17.19 electronic charges are within the Cl^- sphere and the rest of the charge of the Cl^- ion is in the intersphere region.

The possible cause for the low transition energy is believed to be the inaccurate correction potential used in the calculation. For a small cluster the averaged potential defined by Equation (3.13) may be an appropriate approxima-

tion. But for a larger cluster, the deviation of this correction potential from the averaged value in each region may be appreciable. This is especially important in the present calculation of the U center absorption energy. Since the ground state of the U center is in general concentrated in the hydrogen sphere region and the excited state is mainly distributed in the intersphere region, a difference of the correction potentials in these two regions will affect the resulting transition energy almost directly.

The ionic correction potential inside any atomic sphere can be calculated from Equation (3.16), and this potential inside the hydrogen sphere is -8.46/d Ry. The correction potential in the intersphere region can be calculated by Equation (3.17). Since the averaged correction potential inside the cluster region has been calculated for this twenty-center cluster (see Table 3.3), one can use this potential to replace the $V_I(o)$ term in Equation (3.17). This will give a more accurate correction potential for the intersphere region (because of the fact that the parts of the surrounding ions inside the "outer sphere" of the cluster are excluded in the calculation of the averaged correction potential) and this correction potential calculated in the present case is -7.7/d Ry.

Using the correction potential for each region discussed above, one can see that the difference of these potentials between the intersphere region and the hydrogen region is

about 0.13 Ry. Thus, this correction potential for the cluster is expected to give a better U center absorption energy than the previous two calculations. The charge inside the Cl^- sphere is expected to increase also. A calculation using this ionic correction potential for each region has not yet been done.

The twenty-eight-center cluster model shown in Figure 2.3 has also been used for the U center calculation in KCl. In this cluster the hydrogen ion is surrounded by three shells of ions. The first shell consists of six K^+ ions and the second shell consists of twelve Cl^- ions and the third shell consists of eight K^+ ions. The radii used for the atomic spheres and the α values used in various regions are the same as those used in the smaller cluster calculations.

A transition state calculation using this large cluster has been carried out. In the calculation the averaged correction potential given in Equation (3.13) is used. The calculated U center absorption energy is 0.48 Ry which is about 12% higher than the observed value.

In this large cluster transition state calculation, the hydrogen a_{1g} levels of both spins are below the group of levels which arise from the chlorine 3p states, while in the previous twenty-center cluster calculations the hydrogen a_{1g} level with spin up (occupation number is 0.5) is above the chlorine 3p levels and the other hydrogen a_{1g} level is below.

Furthermore, the potentials in various atomic spheres are found to be deeper in the twenty-eight-center case than in the twenty-center case with different magnitude. Thus, large differences are found between the two cluster calculations in potentials and eigenvalues. This is also shown in the calculated U center absorption energies. The reason for the fluctuation of the calculated energies from small cluster calculation to the large cluster calculation is believed to be the use of a constant correction potential inside the entire cluster and also the use of a constant potential in the intersphere region. As mentioned before, the ionic correction potential for each region of the cluster can be found using Equation (3.16) and Equation (3.17). Thus, it is interesting to see the effects of this form of the correction potential used in the calculation.

A twenty-eight-center cluster calculation of the ground state of the U center using the above mentioned correction potential has been done and the results show no spin-polarized effect in the eigenvalues and potentials as would be expected in a closed shell system. The diagram of the calculated eigenvalues is shown in Figure 4.4. The U center ground state is an a_{1g} orbital arising from the hydrogen 1s state with energy equal to -0.545 Ry. Below this level there is a group of fifteen levels (see Appendix B) from the second nearest-neighbor (2nn) Cl^- 3p levels. These levels will form the valence band in a band picture of the crystal when

more and more ions are added to the cluster under consideration. The discussion of this valence band and comparison with other calculations and experimental data will be given in section 4.5. Below the valence levels, the first group near -1.34 Ry consists of ten levels which arise from the 3nn K^+ 3p levels. The width of this group of levels is very narrow because of the relatively small interactions with other states outside this group. Between -1.42 Ry and -1.48 Ry there are twelve levels. Five of them are from the 2nn Cl^- 3s levels and the rest are from the 1nn K^+ 3p levels. Those orbitals mainly concentrated in the 1nn K^+ ions have somewhat higher energy as compared to those concentrated in the Cl^- ions. Since these levels are close in energy, they are actually a mixture of the functions from the two groups of ions. Several unoccupied orbitals are also shown in Figure 4.4. The lowest of the unoccupied states is an a_{1g} orbital. For a U center transition, the lowest unoccupied t_{1u} orbital is the first allowed excited state.

The calculated electronic charges in each region of the present cluster are shown in Table 4.7. In the same table the potential near the boundary of each atomic sphere is also given. As one can see, these potentials are approximately the same for the atomic spheres. This indicates that the correction potentials for the atomic spheres calculated from Equation (3.16) are adequate. For the case of KCl the correction potentials used in the intersphere region,

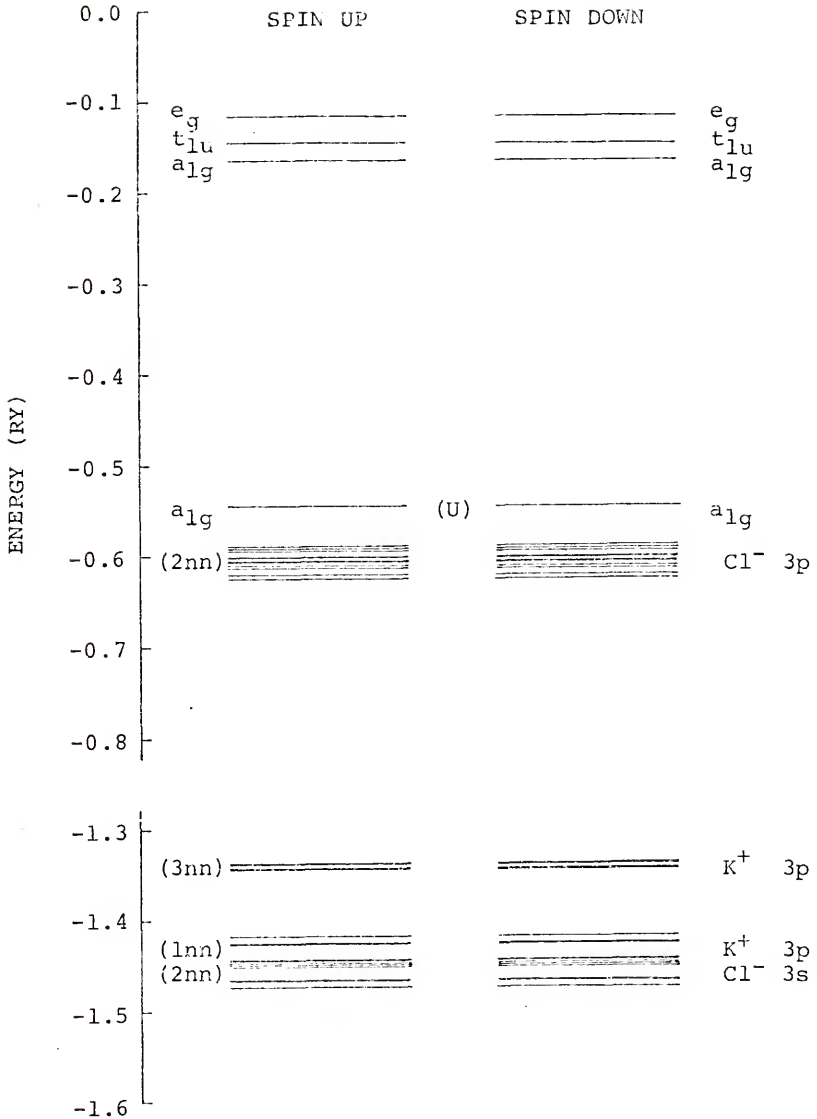

Figure 4.4. The electronic structure of the U center ground state in KCl from the twenty-eight-center cluster calculation.

TABLE 4.7

The electronic charges and the potential in each region from the twenty-eight-center cluster calculation of the ground state of the U center in KCl.

Region	Q	V[a]
Intersphere	9.49	-0.35
Outer	0.05	
H^- (C)	1.74	-0.67
K^+ (1nn)	17.96	-0.79
Cl^- (2nn)	17.33	-0.67
K^+ (3nn)	17.88	-0.65

[a]Values given for sphere regions are the potentials near the sphere boundaries.

hydrogen sphere, 1nn sphere, 2nn sphere and 3nn sphere are 0.125, 0.13, 0.148, 0.079 and 0.23 Ry, respectively. As one can see the use of a constant correction potential for the entire cluster is certainly inappropriate.

A transition state calculation using the twenty-eight-center cluster and a separate correction potential for each region has been tried, but the calculation has not converged due to the difficulty in tracking the hydrogenic a_{1g} orbital which oscillates about the chlorine valence levels. From the correction potentials in the intersphere region and in the hydrogen sphere, it is expected that the calculated U center absorption energy will still be too large. Further discussions on the present correction potential for the cluster will be given in section 4.5 where the cluster calculation is compared with the energy band calculation and other results.

4.2 The F Centers in Alkali Halides

Calculations of the peak energy of the F center absorption band in several alkali halides have been carried out using the spin-polarized MS-Xα-SCF method. In these calculations, the model used for the F center is the eight-center cluster shown in Figure 2.1. A few calculations using the twenty-center cluster and the twenty-eight-center cluster have also been done in the case of KCl.

The F center calculations are similar to the U center

work discussed in the previous section. In fact, the potential from the U center calculation is used as the starting point for the present F center self-consistent calculation. For an F center, the central sphere of the cluster is occupied by an electron. The α value used for the local exchange terms in that region is chosen to be the same as the α value in the surroundings. Thus, for the eight-center cluster, the α values in all regions are the same as Schwarz' α_{HF} values (see Table 3.1) for the first nearest-neighbor cation. For larger clusters (in KCl) the α value in the central sphere is chosen to be 0.72 which is the same value used for the rest of the cluster. The radii used for the atomic spheres are the X-ray corrected radii (see Table 3.2). In most of the calculations the averaged correction potential defined in Equation (3.13) is used.

The ground state of the F center in KCl using the eight-center cluster has been calculated and the eigenstates are shown in Figure 4.5. The diagram is similar to that for the U center eigenstates diagram shown in Figure 4.1. But the spin-polarization effect caused by the unpaired F center electron is clearly shown in the present case. The F center electron occupies an a_{1g} orbital with spin up at -0.183 Ry. The probability for this electron in the central sphere region is about 0.517 from the present calculation and the probability in the intersphere region is about 0.357. Thus, the F center ground state orbital is localized in the anion

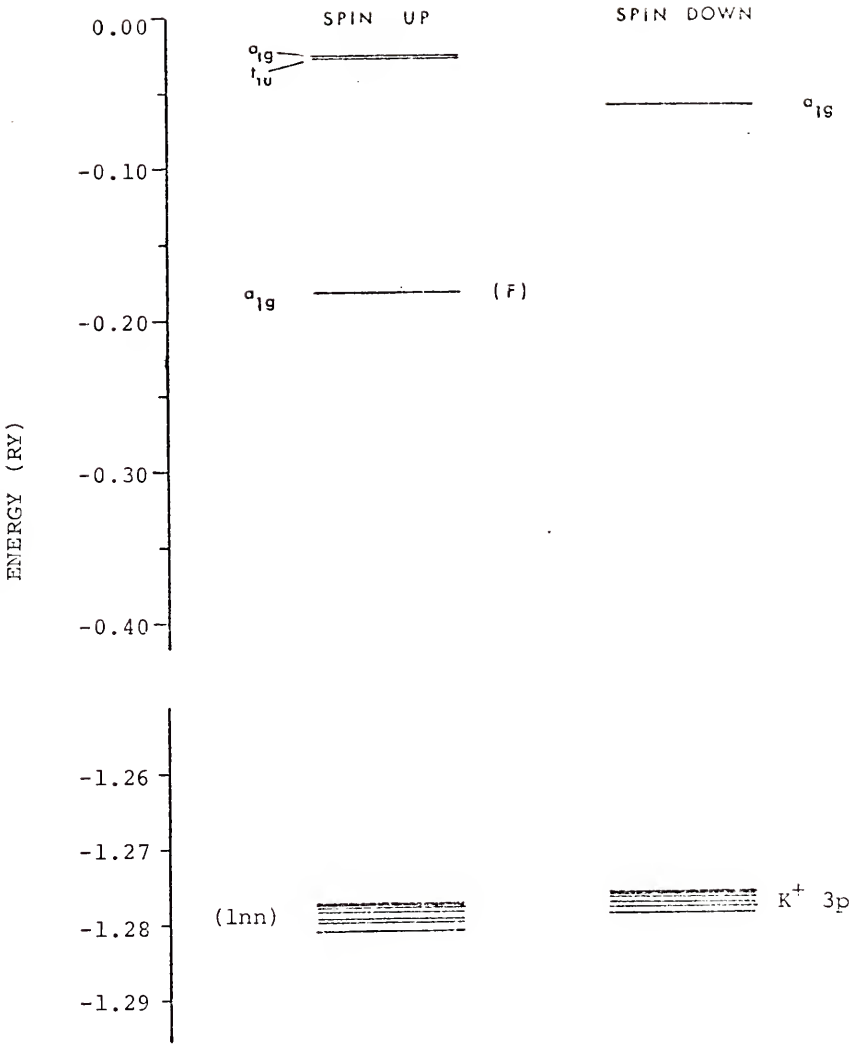

Figure 4.5. The electronic structure of the F center ground state in KCl calculated by using the eight-center cluster.

vacancy although it is not as localized as the U center ground state orbital in the central sphere of the cluster. On the other hand, the first allowed excited state of the F center (which is the t_{1u} orbital with spin up at -0.029 Ry) is relatively extensive. Thus, the probabilities for an electron in this orbital to be found in the intersphere region and outer region of the present cluster are 0.464 and 0.432, respectively. The calculated potential for the spin up electron in the anion vacancy is nearly flat. This gives some justification for the simplified potential well model for the F center mentioned in section 2.4. However, the actual problem is more complicated as one notices from the extensiveness of the excited state wave function of the F center.

The calculated F center absorption energies, using the transition state procedure on several alkali halides, are given in Table 4.8 along with the experimental results and Ivey's values from Equation (2.1). Symbols used in this table are the same as those used in Table 4.2 and are explained in section 4.1. As one can see, the calculated absorption energies in NaCl, NaBr, and KCl are in good agreement with the observed values. In Figure 4.6 the F center energies given in Table 4.8 are plotted against the nearest-neighbor distance of the crystal.

As discussed in the case of the U center absorption, Ivey's relation gives the averaged experimental results and

TABLE 4.8

The optical absorption energies of the F centers in alkali halides calculated by using the eight-center cluster.

Crystal	d	$\varepsilon(a_{1g})$	$\varepsilon(t_{1u})$	ΔE	ΔE_{exp}[a]	ΔE_{Ivey}[b]
LiF	3.800	-0.303	-0.072	0.231	0.375	0.359
NaF	4.370				0.271	0.278
NaCl	5.310	-0.291	-0.093	0.198	0.202	0.194
NaBr	5.630	-0.295	-0.106	0.189	0.174	0.174
KF	5.046					0.213
KCl	5.934	-0.238	-0.065	0.173	0.169	0.158
KBr	6.220				0.152	0.145

All energies are in Rydberg and distance in atomic units.
[a]Rabin and Klick (1960).
[b]Ivey (1947).

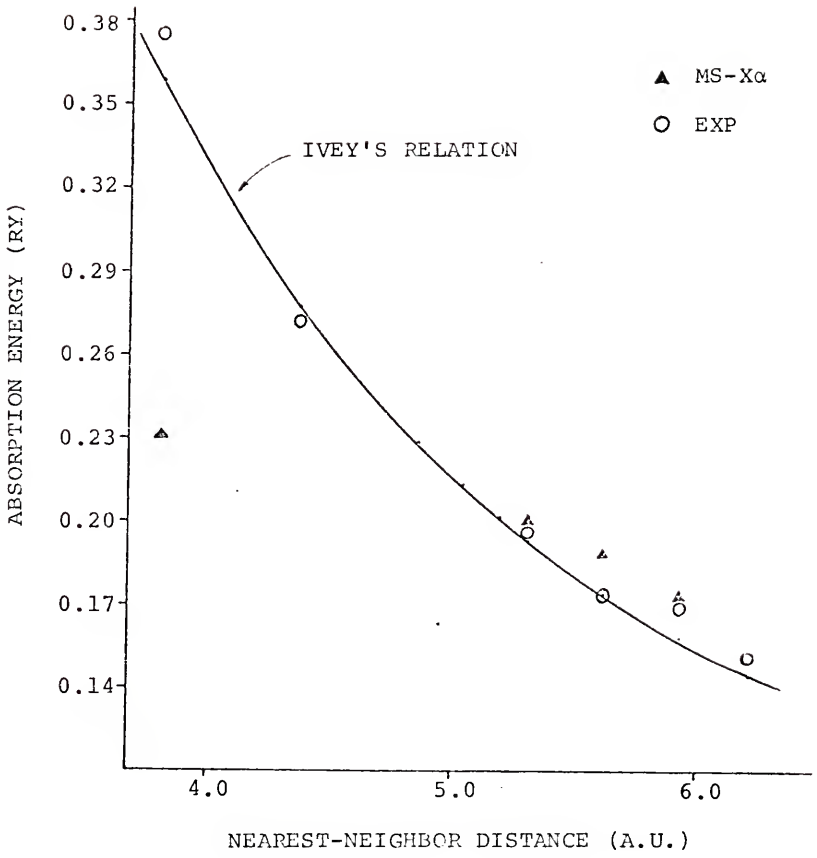

Figure 4.6. The optical absorption energies of the F center as a function of the nearest-neighbor distance of the crystal.

in the present (F center) case, Ivey's relation gives a good approximation to the observed values for all alkali halides shown in the graph. On the other hand, although the present calculated F center energies for most of the alkali halides are in good agreement with the experimental values, the energy calculated for the LiF crystal is 0.231 Ry which is about 0.13 Ry below the experimental value. If one checks the similar U center calculation shown in Figure 4.2, one finds essentially the same differences (compared to Ivey's result) near the small nearest-neighbor distances of the crystal. This indicates that the errors in both cases probably come from the same source. The possible causes are the neglect of ionic overlap (caused by the muffin-tin assumption) in the LiF case and the inadequacy of the correction potential calculated from point charges as the interionic distance becomes small.

Above all, the calculations using the eight-center cluster give good results on the F center absorption energies for most of the ionic crystals. There are other effects associated with the problem that are omitted in the present calculation. For example, the lattice distortion effect and the polarization effect are expected to be more important in the present case than in the U center case. The displacement of cations toward the vacancy will increase the F center transition energy. But the severity of the above mentioned effects is not known. Effects

associated with the exchange parameters and other parameters have been discussed in the previous section; that discussion is also applicable to the present case.

From the ground state calculation of the F center in KCl, the wave function of the F center is obtained. With knowledge of the value of the wave function at the neighboring nucleus, the contact interaction term can be calculated (see, for example, Seidel and Wolf, 1968). In the present case the calculated value is about five times greater than the observed value. The discrepancy may be the consequence of using a finite size cluster.

The electronic structure of the ground state of the F center in KCl has also been calculated in the context of the twenty-center cluster. The averaged value of the correction potential at the centers of all the atomic spheres is used as the correction potential inside the cluster. Thus, $V_I(r)$ equals $-8.32/d$ Ry for all r smaller than R_{out}. Other parameters used in the calculation are the same as those in a similar U center calculation except that the α value for the central sphere is 0.72 in the present case.

The eigenstates calculated from this twenty-center cluster are shown in Figure 4.7. A comparison with the eight-center cluster result shows that the inclusion of the second nearest-neighbor Cl^- ions introduces a band of 15 levels at about -0.55 Ry for each spin. These two bands arise from the atomic 3p levels of the twelve chlorine ions and have the same width (0.047 Ry). The F center electron

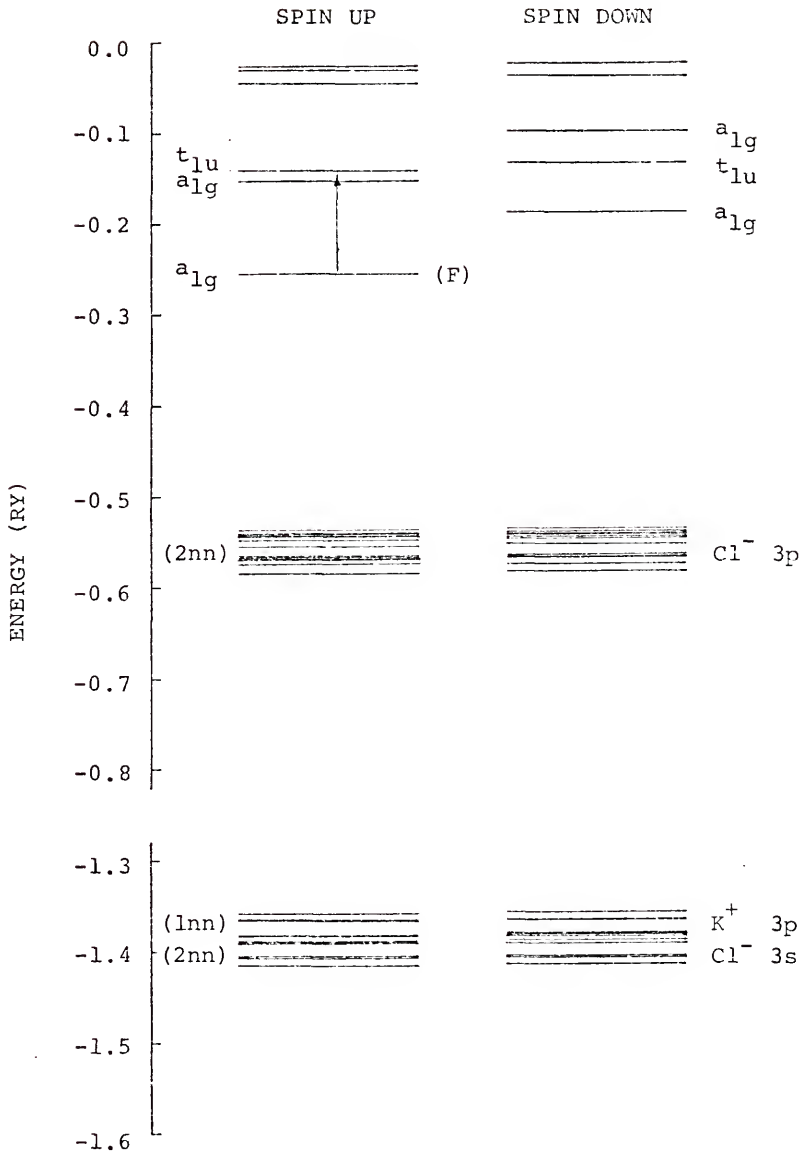

Figure 4.7. The electronic structure of the F center ground state in KCl calculated by using the twenty-center cluster.

occupies an a_{1g} orbital at -0.254 Ry. As one can see from the diagram, the spin polarization effects of the unpaired F electron on the Cl^- 3p band and the K^+ 3p and Cl^- 3s bands below are relatively small as compared to the unoccupied levels. It is also found that the F electron level is closer to the unoccupied levels than in the eight-center cluster case.

A transition state calculation shows that the F center absorption energy is only 0.124 Ry which is about 26% below the experimental value. This is the same sort of situation as that which happens in the twenty-center U center calculation. The addition of the twelve Cl^- ions has apparently pushed the ground state level of the color center too high. It is believed that a more accurate correction potential for the large cluster is essential, especially in the intersphere region.

The ground state of the F center in KCl has also been calculated using the twenty-eight-center cluster. In the calculation, two kinds of correction potential were used. The first is defined in Equation (3.13); it is the averaged correction potential inside the cluster. The electronic structure which results from this calculation is shown in Figure 4.8. The second correction potential is defined in Equation (3.16) and Equation (3.17); in this scheme each region has a separate correction potential. The calculated electronic structure is shown in Figure 4.9. A comparison

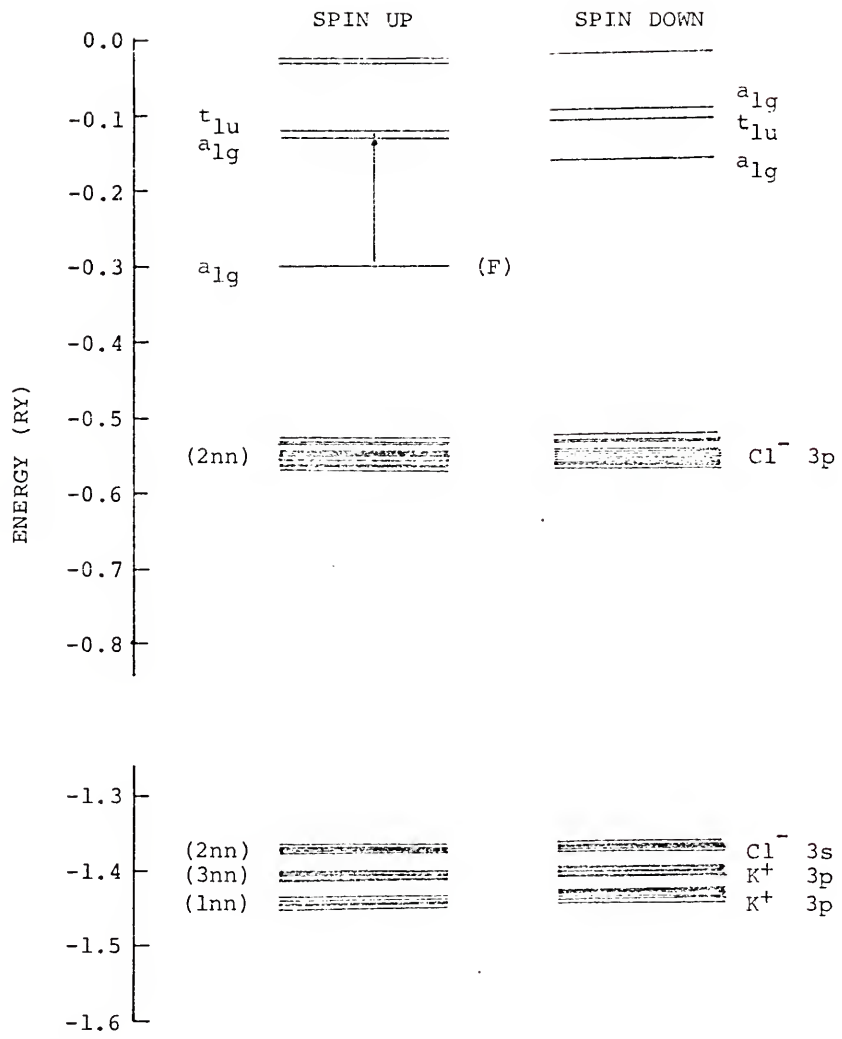

Figure 4.8. The twenty-eight-center cluster calculation of the ground state of the F center in KCl using the averaged correction potential.

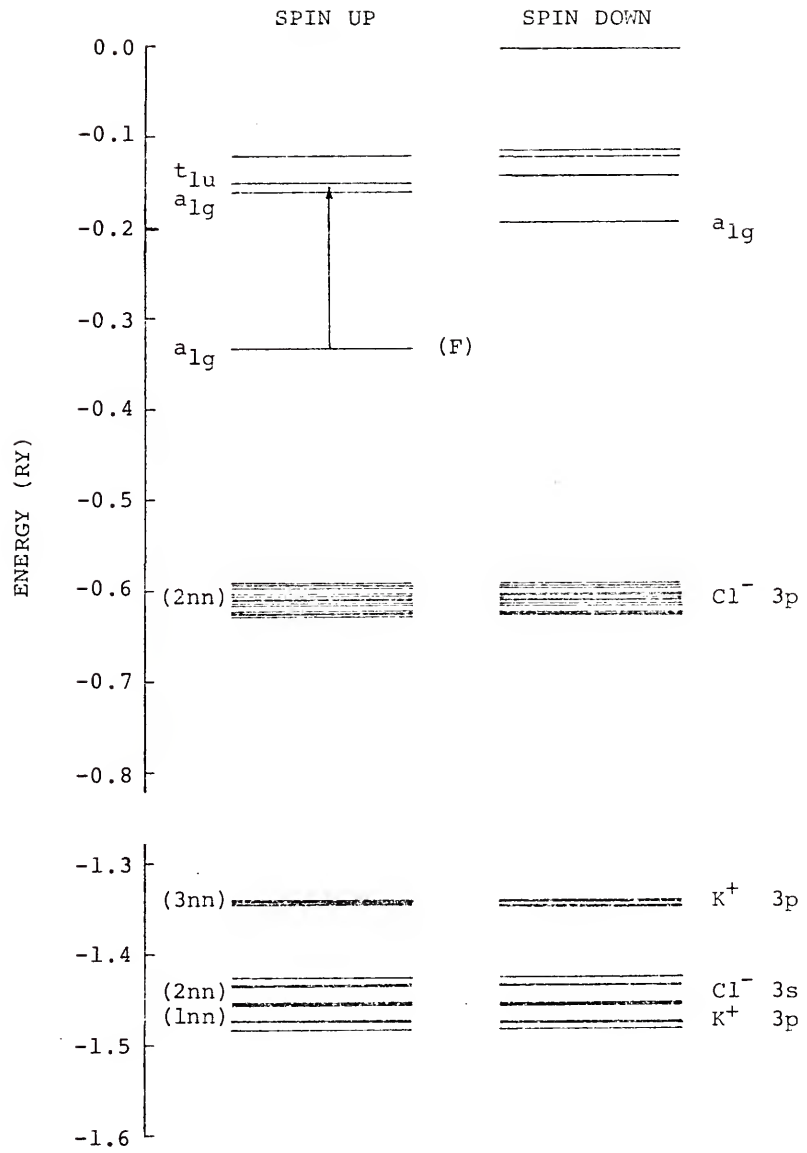

Figure 4.9. The twenty-eight-center cluster calculation of the ground state of the F center in KCl using the separate correction potential.

of the two calculations yields an energy difference between the F center level and the first unoccupied t_{1u} level of 0.178 and 0.182 Ry, respectively, for the two cases. These energies are very close to the F center absorption energy in KCl. The gap between the first unoccupied level and the top of the valence band with spin up is 0.397 and 0.432 Ry respectively. The slightly higher value for the second case is a result of the correction potential used for the 2nn atomic sphere being smaller than those for the central sphere and intersphere region. The effect of the separate correction for each region in the second calculation can also be seen from the lower bands as compared to the first calculation. In Figure 4.8 the highest of the three bands shown is the 2nn Cl^- 3s band whereas in Figure 4.9 the highest band is found to be the 3nn K^+ 3p band.

A comparison of the electronic charges inside each region and a comparison of the calculated potentials for a spin-up electron in the intersphere region and near each sphere boundary (which result from several F center ground state calculations in KCl) are both shown in Table 4.9. The electronic charge inside each ion sphere is seen to increase with the increase of the size of the cluster. On the other hand, the charge in the intersphere region is seen to decrease from the twenty-center case to the twenty-eight-center case. The twenty-eight-center cluster has a total charge of +1, thus, a relatively small correction potential is needed

TABLE 4.9

A comparison of the electronic charges and the potential in each region of the cluster between several F center ground state calculations in KCl.

	8-center	20-center	28-center[a]	28-center[b]
Q_{int}	1.32	10.14	9.78	9.56
Q_{out}	0.07	0.41	0.06	0.05
Q_F	0.56	0.43	0.62	0.61
Q_{K^+} (1nn)	17.85	17.95	17.98	17.97
Q_{Cl^-}(2nn)		17.19	17.29	17.33
Q_{K^+} (3nn)			17.89	17.88
V_{int}	-0.18	-0.42	-0.32	-0.35
V_F[c]	-0.59	-0.58	-0.72	-0.76
V_{K^+} (1nn)[c]	-0.57	-0.73	-0.80	-0.81
V_{Cl^-}(2nn)[c]		-0.56	-0.59	-0.67
V_{K^+} (3nn)[c]			-0.71	-0.65

All energies are in Rydberg.
[a]Use correction potential in Equation (3.13).
[b]Use correction potential in Equations (3.16) and (3.17).
[c]Values given are potentials near the sphere boundary.

in the calculation as compared to that in a smaller cluster calculation. It seems that this large cluster should give better results for the present problem. The calculated F center absorption energy in KCl turns out to be 0.222 Ry and 0.223 Ry using the two different kinds of correction potential mentioned before. These energies deviate from the observed value by about the same amount but opposite direction of that found in the twenty-center calculation. This oscillation of deviation with increasing number of shells can also be seen in the position of the F center level in various diagrams shown in Figures 4.5, 4.7 and 4.8. The difficulty in the present case is traceable to the fact that the F center excited state is not localized while the F center ground state is fairly well localized in the central region of the cluster. Thus, a small deviation of the relative magnitude between the constant potential in the intersphere region and the potential inside the central sphere (which is nearly constant for the case of the F center) will affect directly the calculated transition energy. Clearly, a more accurate evaluation of the correction potential between spheres is needed. One method is to integrate the potential in the intersphere region directly using the method discussed in Appendix A or to use the calculated averaged value inside the cluster combined with Equation (3.17). Estimates have been done and they indicate that the calculated transition energy will be improved in both the twenty-center and twenty-eight-center cases.

From the above discussion, we know that the eight-center cluster calculations give reasonably good results on the F center absorption energies. But the calculation of the contact term for the spin interaction between the F center electron and the neighboring ions indicates that the small size of the cluster has compressed the wave function of F electron and gives a contact term too high compared to the experimental value. Thus, larger clusters are needed to see the improvement on the F center wave function. From the ground state calculation of the large cluster, the contact term is improved, although the value is still too high. On the other hand, the transition energy is found to be worse than that obtained in a small cluster calculation. Improvement of the correction potential has been discussed before, but there are also other difficulties which perhaps are associated with the large cluster. Thus, calculations with a cluster of pure crystal have been done. A study of these calculations can give some information about the present cluster approach. Results of these calculations will be given in section 4.5.

4.3 The U_2 Center in Potassium Chloride

The calculation of the U_2 center in KCl has been done using the cluster shown in Figure 2.2. In this cluster a hydrogen atom is surrounded by four K^+ ions and four Cl^- ions. Since this cluster is electrically neutral, no Watson sphere

is needed in this case. The parameters used in the calculation are the same as those used in the previous U center calculations except for the radius of the interstitial hydrogen sphere which is choosen to be as large as possible without overlapping the other spheres. By this criterion, the radius of the hydrogen sphere is 2.04 atomic units.

The calculated orbital energies of the ground state of this center in KCl are shown in Figure 4.10. The hydrogen ground state is an a_1 orbital with spin up in the present calculation. This hydrogenic a_1 orbital is mixed with the a_1 orbital from the neighboring chlorine ions. From the charge distribution of the orbitals, it is found that the most hydrogen-like a_1 orbital with spin up is below the group of levels from the Cl^- 3p levels while the unoccupied hydrogenic a_1 orbital with spin down is above the chlorine levels. Thus, in this spin-unrestricted calculation, we know that the system with two electrons in the hydrogen 1s levels plus a hole in the chlorine 3p levels has a higher energy than that which has filled chlorine 3p levels and one electron in the hydrogen 1s level. This situation was unclear from the energy considerations of Cho et al. (1966), although the same conclusion was reached.

In finding the excitation energy of this center, there are two possible forms of transition. The first possibility is an electron excited from the highest occupied a_1 symmetry orbital, which is a mixture of the hydrogen 1s level and the

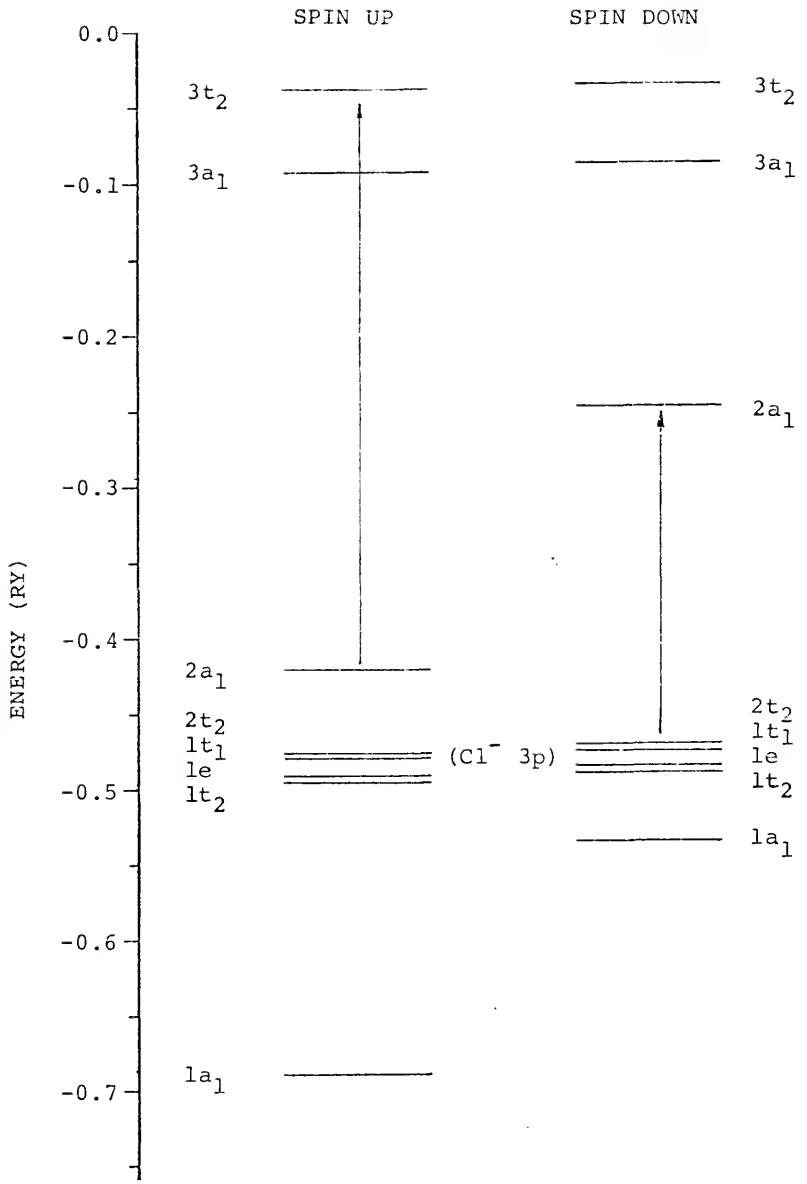

Figure 4.10. The electronic structure of the ground state of the U_2 center in KCl.

neighboring Cl^- 3p levels, to the first unoccupied t_2 orbital. The second possible form of excitation is to excite an electron from the highest occupied spin down t_2 orbital, which is an orbital concentrated on the four Cl^- ions, to the unoccupied hydrogen a_1 orbital. The excitation energies calculated from these two kinds of transition are 0.395 and 0.213 Ry, respectively. Comparing these results to the experimental U_2 absorption energy, 0.387 Ry (Fischer, 1967), one finds that the first form of transition is likely to be the process. In most of the previous calculations on optical transitions in a U_2 center (Mimura and Uemura, 1959; Hagston, 1971), the absorption process was thought to be a charge transfer which is equivalent to the second form of the transition in the present calculation. There is no direct proof of this charge transfer process in a U_2 center absorption. In order to see the effect of the possible lattice distortion around the hydrogen atom upon the transition energy, a calculation of the charge transfer process with the Cl^- ion and the K^+ ion displaced outward and inward, respectively, along the line joining the ion and the hydrogen atom was carried out. The result shows an even smaller energy for the U_2 center absorption. Thus, from the present calculations the process of charge transfer cannot account for the observed absorption energy, and the process with an electron excited from a hybrid chlorine-hydrogen a_1 orbital to a higher state gives a good interpretation for the U_2 optical absorption.

The proton hyperfine interaction of the U_2 center in KCl has been investigated by many workers in this field. Spaeth and Seidel (1971) used the orthogonalized function method and obtained a relative proton hyperfine constant shift $\delta = 9.27\%$, where δ is defined by

$$\delta = \frac{a_{Hi} - a_H}{a_H} \tag{4.1}$$

and a_{Hi} is the proton hf constant for the U_2 center while a_H is the hf constant for a free hydrogen atom. Since the experimentally determined a_{Hi} (1378 MHz) is less than the free hydrogen hf constant (1420 MHz), the relative proton hf constant shift is equal to -3.01% (Spaeth and Sturm, 1970). To improve the calculated value, they tried to take into account the van der Waals interaction between the H atom and its neighboring ions. This has the effect of shifting electron density away from the proton into the outer region of the H atom resulting in a value of $\delta = -9.73\%$. Another model to improve the calculation of δ is to include the crystal field effects using the ligand field model. In this way, Hagston (1970) obtained a value of δ between -1% and -2% in a semi-empirical calculation.

In the present calculation, the proton hf constant is calculated from the spin density at the position of the proton which can be calculated from the following expression:

$$\rho(\vec{r}) = \sum_{i(\uparrow)} n_i \left| \psi_{i\uparrow}(\vec{r}) \right|^2 - \sum_{j(\downarrow)} n_j \left| \psi_{j\downarrow}(\vec{r}) \right|^2 \tag{4.2}$$

where n_i is the occupation number of the ith state and $\Psi_{i\uparrow}(r)$ is the wave function of the ith state at position $\vec{r}$. The summation of i is over all states with spin up and the summation of j is over all states with spin down. Using the spin density at the proton, the calculated δ is equal to -4.5% which is in fairly good agreement with the experimental value.

The calculation of the hf contact term at the nuclei of the Cl^- and K^+ ions has also been done using the spin density obtained from Equation (4.2). Comparing with the experimental results the calculated hf contact term for the Cl^- ion is overestimated and that for the K^+ ion is underestimated and is negative. In order to see the effect on the distribution of the spin-polarization due to a particular choice of the cluster, a different cluster for the U_2 center in KCl was used. This cluster has a K^+ ion at its center with six Cl^- ions surrounding it and also has a hydrogen atom located at (d/2, d/2, d/2) of the cluster, where d is the nearest-neighbor distance of the crystal. The structure of the cluster is similar to that shown in Figure 2.1 except that there is an interstitial atom in the present case and the cluster has C_{3v} symmetry. The calculated hf contact term for the K^+ ion in this case is improved and has a value near zero. The hf contact term for the Cl^- ion is lowered. Thus, overall the cluster with C_{3v} symmetry has improved results for the hf contact term compared to the tetrahedral cluster, but the results are not satisfactory. Since in the present calcula-

tion the spin polarization is mainly within the outer sphere of the cluster in contrast with the experimental results that show spin polarization in the third shell of ions, a larger cluster may be used to improve the results. On the other hand, the hf contact term of the nearest-neighbors of the interstitial hydrogen can also be calculated approximately using the one-electron wave function of the unpaired electron from the tetrahedral cluster calculation. The hf contact term at the Cl^- nucleus in the first shell is found to be 18.0 MHz which is roughly comparable to the experimental value of 23.7 MHz. At the K^+ nucleus, the calculated hf contact term is 3.1 MHz and the experimental value is 1.0 MHz. These results are better than the results obtained using Equation (4.2). But the calculated spin density at the proton position using the one-electron wave function is found to be too small. The reason for this low spin density is probably the fact that the hydrogen-like a_1 orbital is mixed with the a_1 orbital from the neighboring Cl^- ions shifting the spin density away from the proton.

4.4 The U_1 Center in Potassium Chloride

The U_1 center is similar to the U_2 center discussed in the previous section except that the interstitial impurity is a negative hydrogen ion in the present case. The study of this center in KCl has been done using the tetrahedral cluster shown in Figure 2.2. A Watson sphere with charge of +1 was used to enclose the whole cluster.

The calculated orbital energies are shown in Figure 4.11. Contrary to the case of the U_2 center, both of the two hydrogenic a_1 orbitals are above the group of five levels arising from the Cl^- 3p levels. The optical absorption process in this case is thought to be an electron excited from the hydrogenic a_1 orbital to the first unoccupied t_2 orbital. The transition state calculation has been done and shows a transition energy of 0.18 Ry. There are a few experimental measurements of the absorption band of the U_1 center in KCl (Delbecq et al., 1956; Rolfe, 1958), but the peak of this band generally is not clearly defined. It is estimated that the peak of the absorption band is at about 0.32 Ry and the edge of this band is about 0.26 Ry.

In the case of this interstitial impurity, the interaction between the hydrogen ion and the neighboring ions is believed to be greater than that of the previously discussed centers. Consequently, the displacement of ions with respect to their equilibrium positions is more important. Thus, two more calculations with displacementswere carried out. In these calculations, the chloride ions were allowed to displace outward along the cubic diagonals and the potassium ions were allowed to displace inward along the cubic diagonals. The hydrogen-like level was found to shift down because of the relaxation of ions surrounding it, and the resulting transition energies were 0.22 Ry and 0.25 Ry with the ions displaced approximately 5% and 8% of the nearest-neighbor

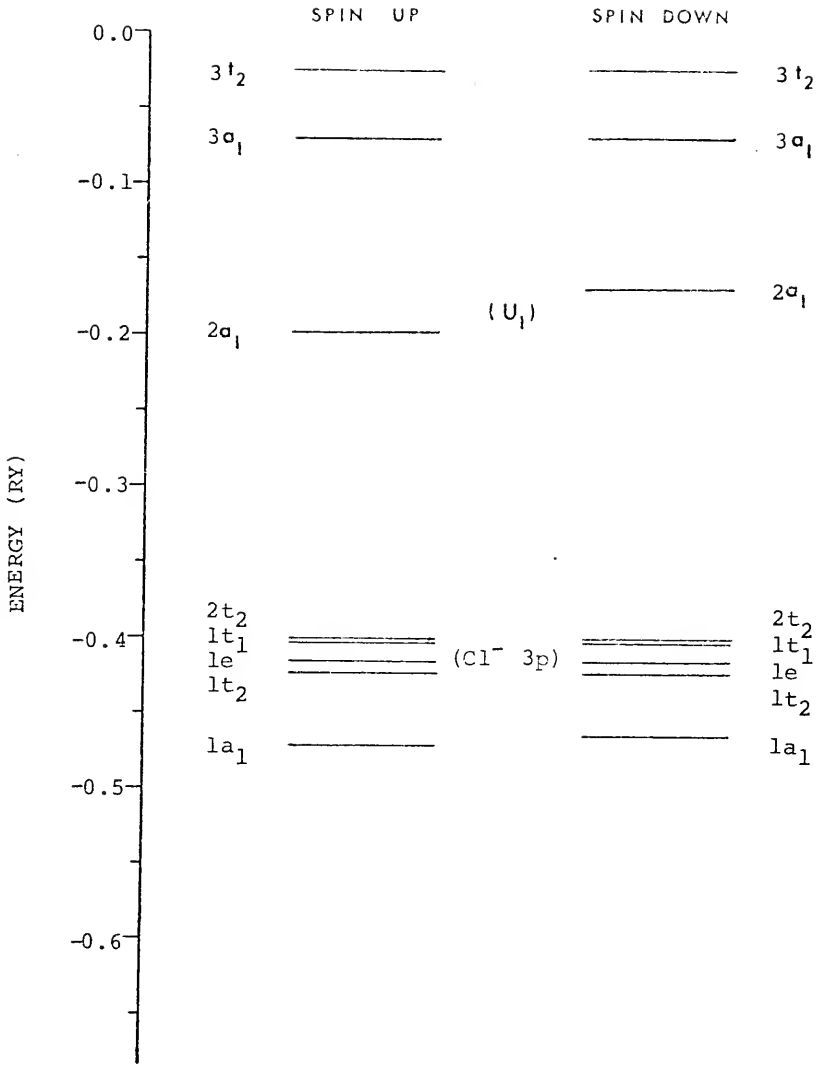

Figure 4.11. The electronic structure of the ground state of the U_1 center in KCl.

distance from their crystal equilibrium positions, respectively.

Thus, from the above results, we know that the displacement of the neighboring ions of the hydrogen played an important role in the U_1 center structure. Since the actual amount of displacement or other distortions of the crystal lattice are not known, we can only qualitatively understand the problem. For more accurate calculations, the polarization effect due to the extra electron on the hydrogen and the more general form of potential must be considered.

4.5 Cluster Calculation of a Pure KCl Crystal

In the previous sections of this chapter we have discussed the calculation of several color center problems using clusters of several different sizes. In section 3.5 we have also discussed the correction potential needed to simulate the potential which arises from the rest of the crystal when the cluster is embedded in the solid. From the calculations on U centers and F centers we know that the orbital energies of the cluster are affected by the correction potentials which are calculated approximately from point charges. It is interesting to compare the electronic structure from a calculation on a pure alkali halide crystal using the present cluster method with that from an energy band calculation or experimental data, e.g., band gap, band width, etc. of a pure crystal. In this way some insight

about the present cluster method can be obtained.

The ground state calculation of the eight-center cluster in KCl, which consists of a Cl^- ion in the center with sex K^+ ions surrounding it (see Figure 2.1), has been done using the non-spin-polarized MS-Xα-SCF method with the same parameters used in the similar F center calculation. The orbital energies calculated are shown in Figure 4.12. The Cl^- 3p level in this case is a t_{1u} state at -0.58 Ry and the lowest unoccupied level is an a_{1g} state at -0.05 Ry. Thus, the difference in energy between these two states is 0.53 Ry. This energy is close to the experimental value, 0.63 Ry, of the band gap in the KCl crystal (Roessler and Walker, 1968). If the states were Bloch states, the above calculated energy difference between the occupied and the unoccupied levels would be the calculated energy gap of the crystal. But in the present cluster calculation the occupied orbitals are quite localized. Thus, there is a significant effect on these orbitals in an optical transition. In other words, we need to use the transition state calculation to find the energy gap of the crystal. This was done and the transition energy from the chlorine t_{1u} orbital to the first unoccupied a_{1g} orbital was found to be 0.64 Ry which is in excellent agreement with the observed energy gap.

As one can see from previous sections, the present eight-center cluster also gives excellent results on the U center and the F center absorption energies in KCl. Therefore, even though in comparison with the experimental values

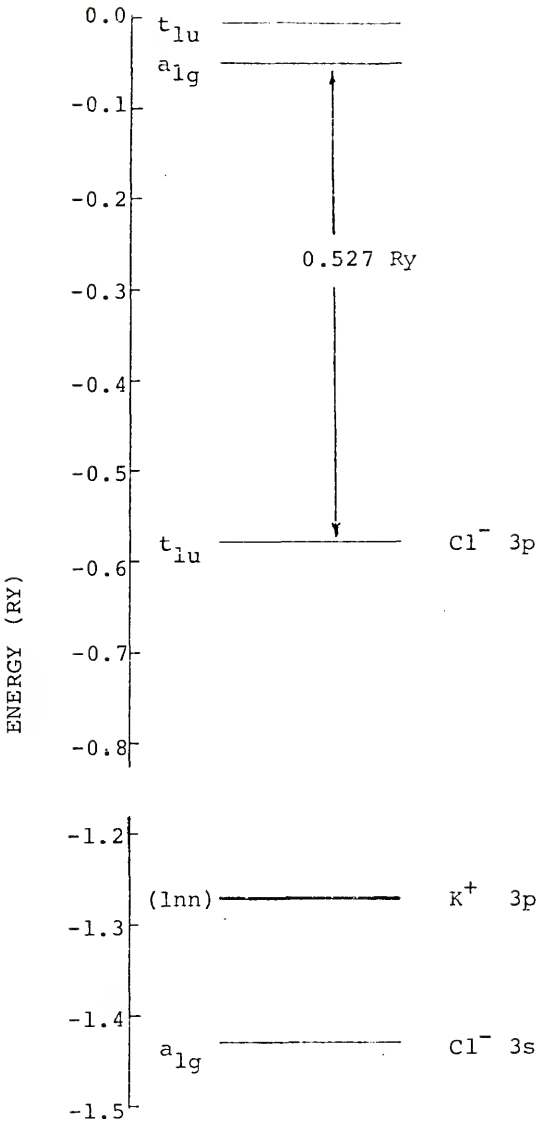

Figure 4.12. The ground state electronic structure of the $Cl^-K^+_6$ cluster.

the U center and F center results for the other crystals are not as good as those in KCl, the consistency in predicting energies of various cases in KCl does indicate that the present cluster approach to the impurity problems is very promising. In view of the results on U center and F center in all crystals, the present success in the KCl crystal may be regarded as accidental. But with the more accurate evaluation of the correction potential and some improvements of the method, the situation may change for all crystals.

Part of the eigenvalues obtained in the previously discussed eight-center cluster calculation have been shown in Figure 4.12. If we take the lowest unoccupied a_{1g} level as the reference of the energy scale, the relative energies of the orbitals from the cluster calculation are given in Table 4.10. In this table, we have also given a set of experimental energy levels of the KCl crystal with energies measured from the bottom of the conduction band. These energies are determined by means of electron spectroscopy with the elimination of the relativistic effects (see Table 6.1 in Slater, 1974). These two sets of energy levels are in good agreement with each other. As we have discussed previously, only the result from the transition state calculation can be compared directly with the experimental value. Thus, the actual calculated levels from a transition state calculation are expected to be lower than those shown in Table 4.10. This should give better agreement with the experimental

TABLE 4.10

A comparison between the relative orbital energies from the eight-center cluster calculation and the experimental energy levels of the KCl crystal.

	8-center[a] (Ry)	Exp.[b] (Ry)
Cl^- 3p	-0.53	-0.61
Cl^- 3s	-1.38	-1.39
K^+ 3p	-1.23	-1.50
K^+ 3s	-2.41	-2.68
Cl^- 2p	-13.93	-14.79
Cl^- 2s	-18.23	-20.31
K^+ 2p	-20.55	-21.78
K^+ 2s	-25.65	-27.54
Cl^- 1s	-201.08	-206.52
K^+ 1s	-257.40	-263.78

[a]Energies measured from the lowest unoccupied a_{1g} level.
[b]Energies measured from the bottom of the conduction band with the elimination of the relativistic effects. Values are taken from Table 6.1 in Slater (1974).

value. On the other hand, the relative positions of the chlorine levels and the potassium levels are noticed to be different from those of the experimental values. This may come from the fact that the correction potential, which is an averaged value inside the cluster, is not accurate for some part of the cluster. This may also be a result of using the cluster method. In order to investigate these problems, a large cluster has been used to calculate the electronic structure of the pure KCl crystal.

In this twenty-eight-center cluster calculation of the KCl crystal, we have used two different correction potentials. The first is the averaged correction for the whole cluster calculated from Equation (3.13). The other uses a separate correction for each region, calculated from Equations (3.16) and (3.17). The ground state of this large cluster of KCl has no effect of spin polarization and the results for the electronic structure of the two calculations using different correction potentials are shown in Figure 4.13 and Figure 4.14. These two diagrams are very similar except that the ordering of some lower bands are different. If we compare these two diagrams with the small cluster result shown in Figure 4.12, we find that an additional band which consists of 15 levels from the second nearest-neighbor (2nn) Cl^- 3p levels is at about -0.6 Ry and there is also a band from the 2nn Cl^- 3s levels and band from the 3nn K^+ 3p levels in the present large cluster calculation. As one can see from Figure 4.13, the t_{1u} level arising from the

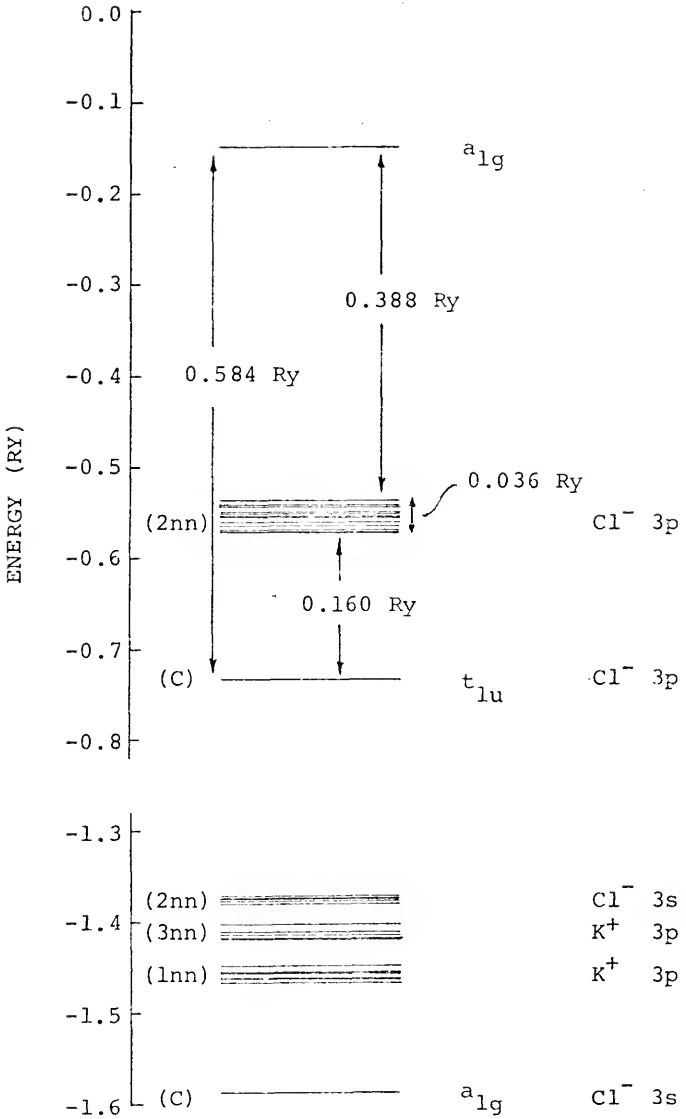

Figure 4.13. The ground state electronic structure of the twenty-eight-center cluster in KCl using the averaged correction potential.

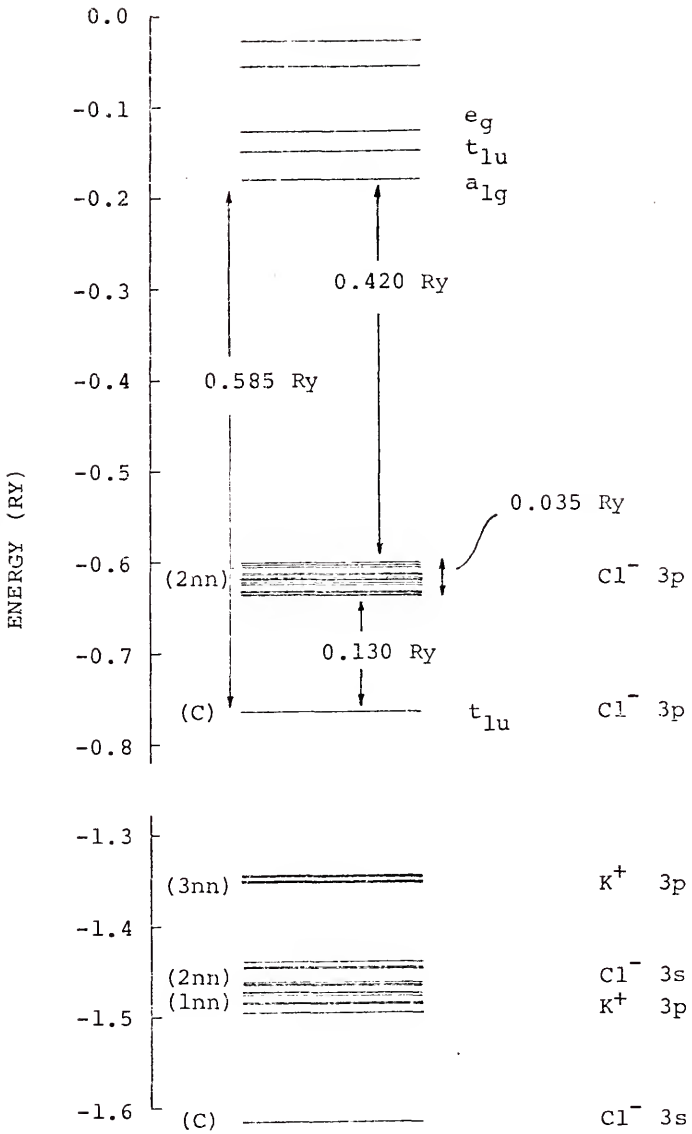

Figure 4.14. The ground state electronic structure of the twenty-eight-center cluster in KCl using the separate correction potential.

central Cl^- 3p level is separated from the band from the 2nn Cl^- 3p levels by about 0.16 Ry. Apparently, the eigenvalues obtained from this cluster calculation do not resemble the band picture from a crystal calculation in which all Cl^- 3p levels form the valence band of the crystal. With the use of separate correction potential for each region of the cluster, the result shows a separation of 0.13 Ry between the lowest level of the 2nn Cl^- 3p band and the central chlorine t_{1u} level. Thus, using this second correction potential the result is improved, but these levels are still far from forming a single valence band. Since most of the occupied orbitals are quite localized in the atomic spheres, this separation should be related to the difference of the potentials of these inequivalent Cl^- spheres.

In Table 4.11 we give the potential of the atomic sphere near its boundary for the two different large cluster calculations. In the first calculation the correction potential inside the cluster is a constant, namely, 0.167 Ry for an electron. Comparing the potentials on the central Cl^- sphere and the 2nn Cl^- sphere, one finds the difference to be 0.25 Ry. The potential difference for the 1nn K^+ sphere and the 3nn K^+ sphere is only 0.1 Ry. In the second calculation, we find that the difference between the inequivalent Cl^- spheres is decreased to 0.20 Ry. But the difference between the inequivalent K^+ spheres is increased to 0.18 Ry.

TABLE 4.11

A comparison of the electronic charges and the potentials in the two different twenty-eight-center cluster calculations of the KCl crystal.

	Av. corr. pot.[a]	Sep. corr. pot.[b]
Q_{Cl^-} (C)	17.45	17.45
Q_{K^+} (1nn)	17.98	17.97
Q_{Cl^-} (2nn)	17.29	17.33
Q_{K^+} (3nn)	17.89	17.88
Q_{int}	9.93	9.70
Q_{out}	0.06	0.05
V_{Cl^-} (C)[c]	-0.85	-0.88
V_{K^+} (1nn)[c]	-0.82	-0.83
V_{Cl^-} (2nn)[c]	-0.60	-0.68
V_{K^+} (3nn)[c]	-0.71	-0.65
V_{int}	-0.32	-0.36

All energies are in Rydberg.
[a]Calculated from Equation (3.13).
[b]Calculated from Equations (3.16) and (3.17).
[c]Values given are potentials near sphere boundaries.

The potential on various sphere boundaries has shown a gradual increase from the inner part to the outer part of the cluster in the second case. Thus, the major factor for the separation of components of various bands in the present result is probably from the cluster method itself instead of the correction potential that is used. In the calculation an outer sphere is used to enclose the whole cluster and the potential outside this outer sphere approaches zero rapidly as the distance increases. Now, the potential outside the cluster is relatively high compared to that inside the cluster. This potential barrier in turn affects the wave function inside the cluster, so that the final calculated potential inside is, in fact, affected by the potential outside. Thus, a higher potential for an ion sphere belonging to the outer shell of the cluster, as compared with a similar ion sphere belonging to the inner shell, is not surprising.

The width of the band arising from the 2nn Cl^- 3p levels is found to be 0.036 Ry and 0.035 Ry in Figures 4.13 and 4.14, respectively. These values are comparable to the valence band width in KCl, 0.039 Ry, calculated by Perrot (1972) using the APWHF method. Other calculated values are 0.057 Ry by Kunz (1968) using the OPW method and 0.060 Ry by De Cicco (1967) using the APW method. The experimental valence band width in KCl is found to be 0.024 Ry if one uses the half-width criterion on the experimental

result of Parratt and Jossem (1955). As to the energy gap obtained in the two large cluster calculations, we find that the differences between the first unoccupied a_{1g} level and the highest allowed level in the 2nn Cl^- 3p band are 0.39 Ry and 0.42 Ry in those two calculations. These energies are smaller than the eigenvalue difference (0.53 Ry) obtained in the eight-center calculation. The calculated energy gap of the solid using the transition state calculation is expected, therefore, to be smaller than the experimental energy gap. However, this is not surprising as we know that the potential and localized orbitals in the 2nn Cl^- sphere have higher values than those in the central Cl^- sphere. Thus, we may use the central Cl^- levels to find whether the calculated energy gap is close to the experimental value. In the two large cluster calculations, the energy differences between the central chlorine t_{1u} level and the lowest unoccupied a_{1g} orbital are 0.58 Ry. These values are closer to the experimental energy gap (0.63 Ry), but with a transition state calculation the calculated interband transition energy is expected to be too high. This can be seen from the eight-center cluster case in which the difference between the occupied and unoccupied eigenstates is 0.527 Ry and the calculated energy gap is 0.64 Ry. Thus, we expect that the calculated energy gap from the large cluster calculation is about 10% or 0.06 Ry higher than the experimental value. This is consistent with the similar F

center calculation in which the F center absorption energy in KCl is found to be about 0.05 Ry higher than the observed value. This consistency in finding the transition energy off by nearly a constant indicates that the correction potential can also be determined semi-empirically by calibrating the cluster results with the experimental data for a pure crystal. This is expected to be relatively simple since most of the orbitals are localized in the atomic spheres, while the excited state is spread mainly in the intersphere region. In any case, the present correction potentials used in the twenty-eight-center cluster still need to be improved. The boundary condition of the cluster method discussed before is believed to raise the outer part of the potential of the cluster. It is also possible that the potential in the intersphere region is being affected. The extent of this surface effect is unknown since there are other effects involved. First, the correction potential is calculated with the assumption that all cations and anions can be treated as positive and negative point-charges. From the charge distribution obtained in the present large cluster calculation which gives only 17.45 electronic charges in the central Cl^- sphere and about 17.30 in the 2nn Cl^- sphere (see Table 4.11), one knows that the correction potential presently used is somewhat different from the actual crystalline potential. Ellis et al. (1966) have developed a spherical harmonic expansion for the correction

potential on clusters removed from a cubic crystal using the free ion charge densities. The potential is separated into the point-ion and overlap contributions. They applied this expansion to the $(NiF_6)^{4-}$ cluster in $KNiF_3$ and showed that the potential for the central ion is essentially flat and the potentials for the ligands are more rapidly varying due to the superposition of point-ion and overlap effects. In the neighborhood of the ligands, they find that the overlap effects are of the order of 10% of the potential. Thus, in the present large cluster the deviations from the point-ion potential for the 2nn and the 3nn ions are expected to be important. Another approximation is the use of the muffin-tin form of the potential. Since there are about ten electronic charges in the intersphere region in the large cluster calculation, the use of a constant potential in that region probably has an appreciable effect on those orbitals which have significant density in that region. In the present case, these orbitals are those which come from the Cl^- 3p levels. The extent of this effect still needs to be investigated.

CHAPTER V

CONCLUSIONS

The main purpose of this dissertation is to study the electronic structure and to calculate the optical absorption energies of the U center and other related color centers by using the spin-polarized MS-Xα-SCF method. In general, the ground state orbitals of these color centers are found to be quite localized and are mainly in the central sphere of the cluster, while the excited state wavefunctions are found to be more extended and are in the intersphere region and the outer region of the cluster. Because of the different nature of the ground state and the excited state orbitals, the energies of these two states are affected by the crystalline potential differently. Thus, in finding the transition energies of various cases, the proper correction potential for the cluster is essential.

Using the eight-center cluster, the optical absorption energies of the U center and the F center in several alkali halides are found to be in good agreement with the experimental values. But in the case of the LiF crystal, the calculated energies are consistently lower than the experimental or Ivey's values by a constant for both the U center and F center cases. One of the causes for this drop is believed

to be the inadequancy of the correction potential. This difficulty stems from the small interionic distance of the LiF crystal which causes a small error in the point charge assumption to have a relatively large effect on the final results. Another difficulty is the use of the muffin-tin approximation which becomes increasingly inappropriate as the ions draw near one another and begin to overlap. Except for the extreme case of the LiF crystal, the MS-Xα-SCF cluster calculation provides a detailed and efficient method to study the color center and the impurity problems. For a localized transition (in which both the ground state and the excited state are localized), the present method is also expected to give satisfactory results with less dependence on the requirement of an accurate correction potential.

For the U_1 center the present cluster method has some difficulties in obtaining quantitatively good results. This is because the displacement of the ions around the impurity and the overlapping of charge densities between ions become more important. From the comparison between the U_1 center and U_2 center calculations, one can see that one additional electron in this interstitial center has a large effect on the electronic structure of the whole cluster and the calculated U_1 absorption energy is found to be much smaller than the experimental value. The removal of the muffin-tin approximation in the calculation will be a great improvement especially if one needs to consider the distortion

of the lattice quantitatively.

In the process of investigating the applicability of the MS-Xα-SCF cluster calculation to the color centers, large clusters were employed in the calculation. The results on the U center and the F center optical absorption energies are found to oscillate about the experimental values as shells of ions are added to the original eight-center cluster. From the calculations the anion sphere is found in general to have a net charge of less than 0.4 electronic charge, and the rest of the charges of the negative ions are usually distributed in the intersphere region. This indicates that the calculation of the correction potential for the cluster using the point-charge assumption is an approximation which may be appropriate for a small cluster but will start to deviate from the actual crystalline potential in the outer part of a large cluster as well as in the intersphere region of the cluster. These difficulties are accentuated by the use of a muffin-tin potential.

From the comparison between the cluster calculation for a pure KCl crystal and other experimental and theoretical data on the electronic structure of the crystal, the present cluster calculation gives acceptable results for the positions of the energy levels and the width of the valence band. On the other hand, some significant differences are also found, namely, the separation of the similar levels between different groups of ions, and the error in predicting the energy gap in

the large cluster calculation. These differences are actually related to the potential in the cluster which is generally found to increase from the inner part to the outer part of the cluster. One of the possible causes is the cluster method itself, since it uses a potential approaching to zero rapidly outside the cluster. Another possibility is the point-charge correction potential which probably causes an error in the potential near the outer part of the cluster.

In conclusion, the small cluster proved to be useful to study the electronic structure and the optical properties of the color center or impurity problems. It gives excellent transition energies for the U center, the F center and pure crystal in KCl consistently. This implies, in cases where quantitative results are desired, that this method can also be used semi-empirically by comparing with the experimental data or accurate energy band calculations to determine the correction potential used for a cluster in any crystal. With this information, the method can be applied to many defect problems. This is not done in the present calculation since the correction potentials calculated by point charges are found to be adequate for a number of cases. But for the larger clusters, the more accurate calculation of the correction potential (using probably the charge densities of ions) becomes necessary in order to give satisfactory results. The large cluster may be used semi-empirically as discussed above. In any case, the large cluster calculation

can be carried out without difficulty. This can be used to study the cases of more complex defects in solid.

APPENDIX A

THE EVJEN METHOD

The Evjen method (Evjen, 1932) is a direct sum method to evaluate the Madelung constant in an ionic crystal (see Tosi, 1965). In this method, the crystal is divided into the smallest block with four anions and four cations at its corners. Only one-eighth of the charge of each ion is counted as inside that block. By summing the cubic shells composed of those small blocks around the point of interest, a converging series for calculating the electrostatic potential at that point can be obtained.

If the origin is chosen to be at the nucleus of a negative ion, the Madelung constant (α_M) is defined by

$$\alpha_M = \sum_i \frac{q_i/|q_i|}{r_i/d} \qquad \text{(A.1)}$$

where q_i is the charge of the ith ion and r_i is the distance from origin to the ith ion, and d is the nearest-neighbor distance of the crystal. The summation is over all ions surrounding the origin. Using the Evjen method, the Madelung constant is found to be 1.7475646. In Table A.1, the α_M is calculated by including up to the Nth shell which includes a cube of ions with its corners at (±Nd, ±Nd, ±Nd).

Using the same procedure, the electrostatic potential

at any point inside the cluster can be found. A volume average of this potential inside the outer sphere but excluding the space occupied by other ions is calculated by using a uniform three-dimensional mesh of points. In practice, only the first few shells are included in the summation and the calculated correction potentials shown in Table 3.3 are carried out with the inclusion of the seventh shell.

TABLE A.1

The Madelung constant evaluated by using Evjen's method.

N	α_M
2	1.751769133
3	1.747041560
4	1.747721100
5	1.747500502
6	1.747595517
7	1.747547900
8	1.747574382
10	1.747568604
14	1.747565638
18	1.747564977
24	1.747564715
30	1.747564644
40	1.747564610

APPENDIX B

SYMMETRY ORBITALS

When several atoms or ions come together to form a molecule or cluster, the atomic levels of these atoms or ions will split into orbitals which belong to various irreducible representations of the symmetry group describing that molecule or cluster. In a cluster shown in Figure 2.3, atomic levels from different shells of ions will emerge as different sets of symmetry orbitals. The relation between the atomic levels of different shell of ions in that cluster and the symmetry orbitals is shown in Table B.1. In this table, the symmetry orbitals are labeled by the various representations of the O_h group. A similar table (Table B.2) shows the symmetry orbitals in a cluster shown in Figure 2.2 with T_d symmetry.

TABLE B.1

Relation between the symmetry orbitals and the atomic levels in a cluster with the O_h symmetry.

Ion group [a]	No. of ions	Atomic levels	Max. occ.	Symmetry orbitals
C	1	s (ℓ=0)	2	a_{1g}
C	1	p (ℓ=1)	6	t_{1u}
C	1	d (ℓ=2)	10	e_g, t_{2g}
C	1	f (ℓ=3)	14	t_{1u}, t_{2u}, a_{2u}
C	1	g (ℓ=4)	18	a_{1g}, e_g, t_{2g}, t_{1g}
1nn	6	s (ℓ=0)	12	a_{1g}, t_{1u}, e_g
1nn	6	p (ℓ=1)	36	a_{1g}, (2)t_{1u}, e_g, t_{2g}, t_{2u}, t_{1g}
1nn	6	d (ℓ=2)	60	a_{1g}, (2)t_{1u}, (2)e_g, (2)t_{2g}, (2)t_{2u}, t_{1g}, a_{2u}, a_{2g}, e_u
2nn	12	s (ℓ=0)	24	a_{1g}, t_{1u}, e_g, t_{2u}, t_{2g}

TABLE B.1 continued:

Ion group [a]	No. of ions	Atomic levels	Max. occ.	Symmetry orbitals
2nn	12	p (ℓ=1)	72	a_{1g}, (3)t_{1u}, a_{2u}, a_{2g}, (2)e_g, e_u, (2)t_{1g}, (2)t_{2u}, (2)t_{2g}
2nn	12	d (ℓ=2)	120	(2)a_{1g}, (4)t_{1u}, a_{2u}, a_{2g}, a_{1u}, (3)e_g, (2)e_u, (3)t_{1g}, (4)t_{2u}, (4)t_{2g}
3nn	8	s (ℓ=0)	16	a_{1g}, t_{1u}, a_{2u}, t_{2g}
3nn	8	p (ℓ=1)	48	a_{1g}, (2)t_{1u}, a_{2u}, e_g, e_u, t_{1g}, t_{2u}, (2)t_{2g}
3nn	8	d (ℓ=2)	80	a_{1g}, (3)t_{1u}, a_{2u}, (2)e_g, (2)e_u, (2)t_{1g}, (2)t_{2u}, (3)t_{2g}

[a] See Figure 2.3.

TABLE B.2

Relation between the symmetry orbitals and the atomic levels in a cluster with T_d symmetry.

Ion group [a]	No. of ions	Atomic levels	Max. occ.	Symmetry orbitals
C	1	s (ℓ=0)	2	a_1
C	1	p (ℓ=1)	6	t_2
C	1	d (ℓ=2)	10	t_2, e
C	1	f (ℓ=3)	14	a_1, t_2, t_1
C	1	g (ℓ=4)	18	a_1, t_2, e, t_1
T	4	s (ℓ=0)	8	a_1, t_2
T	4	p (ℓ=1)	24	a_1, (2)t_2, e, t_1
T	4	d (ℓ=2)	40	a_1, (3)t_2, (2)e, (2)t_1

[a] See Figure 2.2. C=central ion, T=the four ions on the vertexes of a tetrahedron.

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Hsi-Ling Yu was born in August 23, 1945 in Chungking, China. He moved with his parents to Taipei in 1947 and attended school there through high school. In September, 1964 he entered the Tunghai University in Taichung and received a Bachelor of Science in Physics in June, 1968. After one year military service in the Army Arsenal, he entered the Graduate School of the University of Florida in September, 1969 and has been pursuing work toward the degree of Doctor of Philosophy since that time.

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